# Total Asymmetric Synthesis of Doubly Branched Carba-hexopyranoses and Amino Derivatives Starting from the *Diels-Alder* Adducts of Maleic Anhydride to Furfuryl Esters

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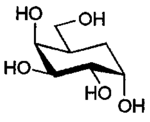
The *Diels-Alder* adducts of maleic anhydride to furfuryl esters were reduced into 7-oxabicyclo[2.2.1]hept-5-ene-1,2-*exo*,3-*exo*-trimethanol (±)-**15** and enantiomerically pure (−)-**15** (*Scheme 1*). The tripivalate of (±)-**15** was converted into (1*RS*,2*RS*,3*RS*,4*RS*,5*SR*,6*SR*)-1,5,6-tris(hydroxymethyl)cyclohexane-1,2,3,4-tetrol ((±)-**23**; *Scheme 2*). Reaction of $BBr_3$ with the triacetate (±)-**30** of (±)-**15** gave (1*RS*,2*RS*,5*RS*,6*RS*)-5-bromo-6-hydroxycyclohex-3-ene-1,2,3-trimethyl triacetate ((±)-**31**) at −78°, and (1*RS*,2*RS*,5*SR*,8*SR*)-2-*endo*-hydroxy-6-oxabicylo[3.2.1]oct-3-ene-5,8-dimethyl diacetate ((±)-**32**) at 0° (*Scheme 3*). Single-crystal X-ray diffraction of (1*RS*,2*RS*,5*SR*,8*SR*)-2-acetoxy-6-oxabicyclo[3.2.1]oct-3-ene-5,8-dimethyl diacetate ((±)-**33**) was carried out. Displacement of bromide (+)-**31** (derived from (−)-**15**) with azide anion gave (+)-**38** which was transformed into (+)-(1*R*,2*R*,5*S*,6*S*)-5-amino-6-hydroxycyclohex-3-ene-1,2,3-trimethanol ((+)-**40**) (*Scheme 4*). Reaction of (±)-**31** with $BBr_3$ at 0°, followed by azide disubstitution led to (1*RS*,2*RS*,5*SR*,6*SR*)-5-amino-3-(aminomethyl)-6-hydroxycyclohex-3-ene-1,2-dimethanol ((±)-**45**). Dihydroxylation of (±)-**38** and further transformations gave (1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*)-5-amino-1,4,6-trihydroxycyclohexane-1,2,3-trimethanol ((±)-**49**) and (1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*)-2,3-dihydroxy-7-oxabicyclo[4.1.0]heptane-2,3,4-trimethanol ((±)-**55**) (*Schemes 5* and *6*). Expoxidation of the 4-nitrobenzoate (±)-**61** of (±)-**38** allowed the preparation of (1*RS*,2*RS*,3*SR*,4*RS*,5*RS*)-5-amino-1,4-dihydroxycyclohexane-1,2,3-trimethanol ((±)-**65**) and of (1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*)-5-amino-4-hydroxy-7-oxabicyclo[4.1.0]heptane-1,2,3-trimethanol ((±)-**67**) (*Scheme 7*). The new unprotected polyols and aminopolyols were tested for their inhibitory activity toward commercially available glycohydrolases. At 1 mM concentration, 34, 30, and 31% inhibition of $\beta$-galactosidase from bovine liver was observed for (+)-**40**, (±)-**65**, and (±)-**67**, respectively.

**Introduction.** – Inositol (cyclohexanehexol) derivatives [1] play a crucial role in signal transduction in living organisms [2]. Their syntheses has stirred a lot of activity recently [3]. Conduritols (cyclohexenetetrols) [4], conduramines (aminocyclohexenetriols) [5], and their epoxides [6] have been of deep interest to the synthetic chemists due to their potential as glycosidase inhibitors [7] or as antibiotics [8]. These systems can be viewed as carba-pentopyranose derivatives [9]. Carba-hexopyranoses ((hydroxymethyl)cyclohexanepolyols) have been synthesized first [10] and then found in Nature [11]. For instance, 5a-carba-$\alpha$-D-galactopyranose (**1**) has been isolated as a weak antibiotic from the fermentation broth of *Streptomyces* species [12]. Valienamine (**2**) is a constituent of agricultural antibiotic validamycin [13], of the $\alpha$-amylase inhibitor acarbose [14], and of the trehalase inhibitors validoxylamine A [15] and salbostatin [16].

Gabosines (*e.g.*, **3**, gabosine A; **4**, gabosine C) are carba-sugars isolated from different *Streptomyces* [17]. Epoxides [18] such as pipoxide (**5**) [19] and crotepoxide (**6**) [20] are natural products showing significant tumor-inhibitory activities; cyclo-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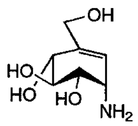
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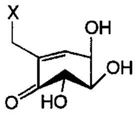
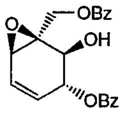

**3** X = H
**4** X = OH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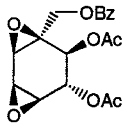
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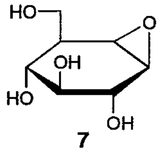
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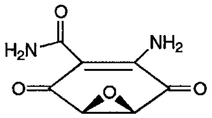
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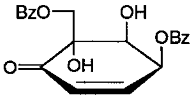
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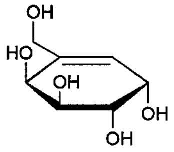
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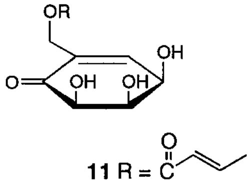
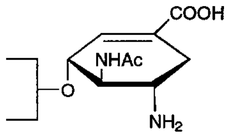

**11** R =
**12** R = H


**13**

phellitol (**7**) isolated from culture filtrates of *Phellinus* sp. [21] and its synthetic stereoisomers [22] are glycosidase inhibitors [23]. Epoxy dione such as **8** is an antibiotic isolated from *Streptomyces* species [24]. The ethanolic extract of the seeds of *Uvaria tonkinensis* (*Annonaceae*) has delivered tonkinenin A (**9**) [25]. Herbicidal MK 7607 (**10**) is manufactured by cultivation of *Curvularia* species [26]. The glyoxalase-I inhibitor **11** has been isolated from the culture broth of *Streptomyces griseosporeus* [27], and its precursor **12** ((–)-KD16-U1) from the culture broth of *Streptomyces filipinensis* [28]. Synthetic carba-sugars are potential leads in all kinds of therapeutic applications. For instance, the potent influenza neuraminidase inhibitor GS 4071 (**13**) has been prepared [29] and shown to be promising for the prophylaxis and treatment of influenza-virus infection [30].

Recently, we disclosed [31] a simple method for the preparation of enantiomerically pure 7-oxabicyclo[2.2.1]hept-2-ene derivative (+)-**14**, precursor in the synthesis of taxol analogues [32]. We envisioned that (+)-**14** and its diastereoisomer, derived from (1*R*)-camphanic acid, could be suitable starting materials to generate families of new types of carba-sugars. We report here our exploratory studies on the conversion of (+)-**14** into tri(hydroxymethyl)cyclohexanepolyols and amino derivatives; some of the reactions presented here represent very short syntheses of these new doubly-branched carbahexoses including conduritol-like systems and their epoxides.

**Results and Discussion.** – Our exploratory studies were carried out starting from racemic triol (±)-**15** [33] (*Scheme 1*). In the case of the synthesis of (1*R*,2*R*,5*S*,6*S*)-5-amino-6-hydroxycyclohex-3-ene-1,2,3-trimethanol ((±)-**40**), enantiomerically pure triol (–)-**15** was used as starting material[1]).

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[1]) For a partial preliminary report, see [35].

*Scheme 1*

(+)-**14** R* = (1'*S*)-camphanoyl

(-)-**15** R = H
**28** R = *t*-BuCO = Piv
**30** R = Ac

*1,5,6-Tris(hydroxymethyl)cyclohexane-1,2,3,4-tetrol*(±)-**23**. Double *exo*-hydroxylation of the alkene moiety of (±)-**15** (*N*-methylmorpholine *N*-oxide, $OsO_4$ (cat.)) gave (±)-**16** which was esterified to pentaacetate (±)-**17** ($Ac_2O$, pyridine, 4-(dimethylamino)pyridine (DMAP) as catalyst; 91% yield) or to pentapivalate (±)-**18** (PivCl, pyridine; 80%) (*Scheme 2*). Pentaacetate (±)-**17** did not react with $BBr_3$ in $CH_2Cl_2$. On heating, slow decomposition was observed. However, the pentapivalate (±)-**18** reacted smoothly with $BBr_3$, already at 0°, giving after aqueous workup ($NaHCO_3$) diol (±)-**19** in 88% yield (*Scheme 2*). The crude reaction mixture did not show any other product. Diol (±)-**19** was protected as bis(methoxymethyl) diether (±)-**20** (97%) or as diacetate (±)-**21** (100%) under standard conditions. Oxidation of diol (±)-**19** with $H_2CrO_4$ produced $\gamma$-hydroxy ketone (±)-**22** (100%). Saponification (MeONa, MeOH, 20°) of pentapivalate (±)-**19** provided heptol (±)-**23**, which was fully characterized as its hexaacetate (±)-**24** (91%, 2 steps). The structures of **16**–**24** were given by their spectral data and their elemental analysis.

The *exo*-face selectivity of the dihydroxylation of **15** was confirmed by the $^1$H-NMR spectra of **16**–**18** which did not show any coupling (< 0.5 Hz) between vicinal proton pairs H–C(4) and H–C(5) [34]. The spectra exhibited coupling constants $^3J(5,6) = 6.0–6.4$ Hz for the *endo* vicinal proton pairs, confirming the *cis* relationship between these protons [34]. The $^1$H-NMR spectra of **19**–**21** and **24** showed coupling constants between vicinal proton pairs of the six-membered ring (H–C(2), H–C(3), H–C(4), H–C(5), and H–C(6) that are all smaller than 5 Hz, in agreement with the proposed structures and conformations (no axial/axial vicinal proton pairs). The $^1$H-NMR spectrum of ketone **22** showed coupling constants $^3J(5,6) = 4.5$ Hz and $^4J(3,5) = 2$ Hz, consistent with the proposed structure and conformation. Its 2D-NOESY data revealed NOEs between one of the protons ($\delta$(H) 4.49, *d*, $^2J = 12$ Hz) of $CH_2$–C(1) with H–C(2) ($\delta$(H): 1.67, *m*) and H–C(3) ($\delta$(H) 2.66, *m*). The other proton ($\delta$(H) 4.49, *d*, $^2J = 12$ Hz) of $CH_2$–C(1) showed NOEs with H–C(6) ($\delta$(H) 5.78, *d*, $^3J = 4.5$ Hz) and H–C(5) ($\delta$(H) 5.66, *dd*, $^3J = 4.5$, $^4J = 2.0$ Hz). This established the *trans* relative configuration of the 1-(pivaloyloxymethyl) substituent with respect to the 6-(pivaloyloxy) substituent. The 2D-NOESY data of **24** confirmed the relative configuration and the conformation shown for this hexaacetate, with NOEs between H–C(6) ($\delta$(H) 2.24, $^3J = 7.6$, 4.9, 5.0 Hz), H–C(4) ($\delta$(H) 5.45, $^3J = 3.9$, 2.8 Hz), and H–C(2) ($\delta$(H) 5.26, $^3J = 3.9$ Hz).

The high yield and high stereoselectivity of the 7-oxa-ring-opening reaction/quenching reaction **18** → **19** is remarkable[2]). It can be interpreted in terms of the formation of cationic intermediate **25A** arising from the *Lewis*-acid-promoted heterolysis of the C(1)–O(7) bond in **18** with participation by the 1-(pivaloyloxymethyl) substituent. Because of the bulk of the pivaloyl group, $BBr_3$ coordination of

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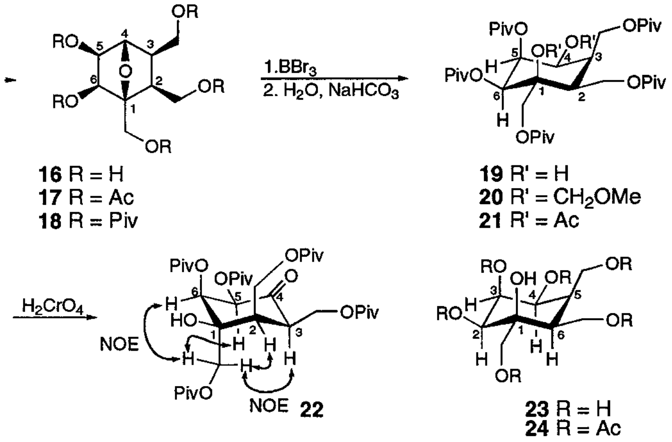
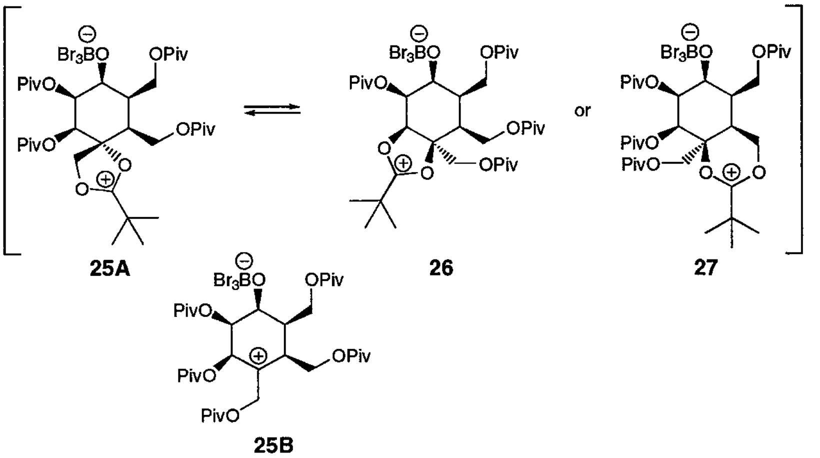
[2]) For other examples of *Lewis*-acid-promoted oxa-ring openings of 7-oxabicyclo[2.2.1]heptane derivatives, see [36].

*Scheme 2*



the ester moieties is less important for the pentapivalate **18** than for the corresponding pentaacetate **17**, thus explaining the fast reaction observed with the former and the lack of reactivity of the latter 7-oxabicyclo[2.2.1]heptane derivative. In the presence of $H_2O$, **25A** is expected to yield a hemiorthoester that rearranges to the 1-epimer of **19** that is not detected by NMR of the crude reaction mixture. Opening of the dioxolanium intermediate **25A** with formation of isomeric tertiary carbenium ion intermediate **25B** is possible, but its reaction with $H_2O$ is expected to give a mixture of **19** and of its 1-epimer, the latter product being preferred under conditions of kinetic control for steric reasons. Although we cannot rule out a direct attack of $H_2O$ at the *quaternary* C(1) center of **25A** to generate **19**, this intermolecular $S_N2$-type reaction looks unlikely. We thus propose that **25A** can equilibrate with intermediates **26** or/and **27** through intramolecular displacements with complete inversion of configuration at C(1). The cationic intermediates **26** and **27** might be more stable than **25A** for reasons of steric hindrance to solvatation, or may react faster than **25A** (for steric reasons) with $H_2O$



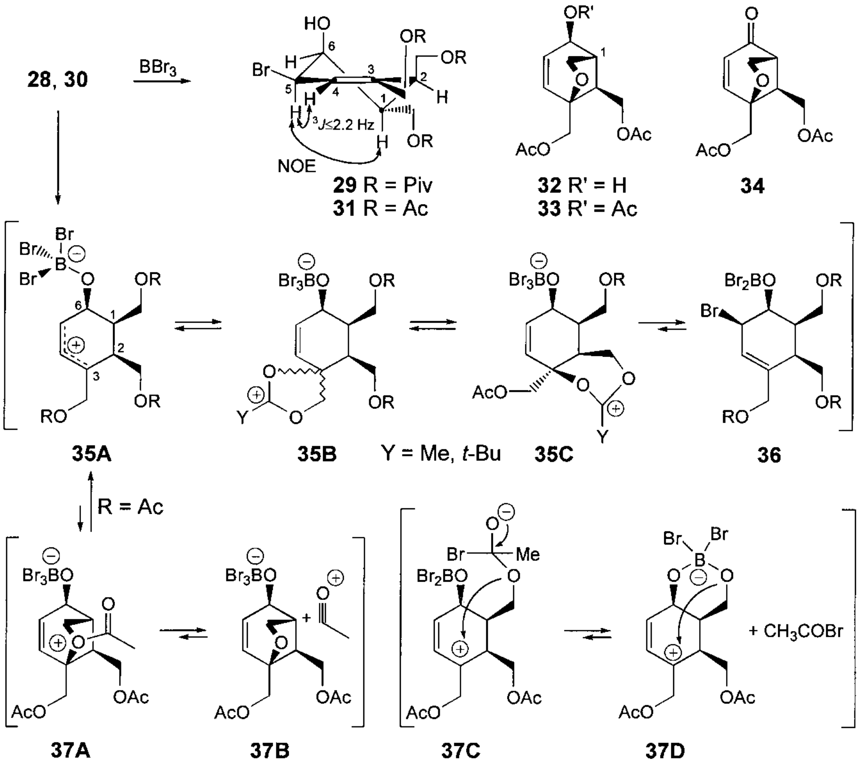
giving the corresponding hemiorthoesters that rearrange to form **19** exclusively. Formation of isomeric tertiary pivalate is prevented for steric reasons (front strain). It is interesting to mention that in the presence of a large excess of $Bu_4NBr$ or of KBr/[18]crown-6 ether, the same product **19** was obtained on treating **18** with $BBr_3$ first, and then with $H_2O/NaHCO_3$. If **25A** should react in a $S_N2$ fashion with $H_2O$ to produce **19**, the corresponding bromide should have been seen in the latter experiments, which was not the case.

*(1*R*,2*R*,5*S*,6*S*)-5-Amino-6-hydroxycyclohex-3-ene-1,2,3-trimethanol(±)-***40** *and Its 3-(Aminomethyl) Derivative* **45**. Esterification of triol (±)-**15** with pivaloyl chloride in pyridine provided (±)-**28** (93%) (*Scheme 1*). Treatment of (±)-**28** with $BBr_3$ ($CH_2Cl_2$, 0°, 5 min, aqueous workup) gave bromohydrine (±)-**29** in 95% yield (*Scheme 3*). Triacetate (±)-**30** (*Scheme 1*) derived from (±)-**15** ($Ac_2O$, pyridine, $CH_2Cl_2$; 95%) reacted with $BBr_3$ already at – 78° in $CH_2Cl_2$ to give the expected bromohydrine (±)-**31** in 95% yield. When the reaction was carried out at 0° using a higher dilution, a second product (±)-**32** was formed and was isolated with a yield of up to 46%. The structures and conformations of (±)-**29** and (±)-**31** were given by their spectral data, especially by their $^1H$-NMR spectra that shared similarities for their coupling constants between vicinal proton pairs.

Coupling constants $^3J\,(4,5) < 1$ Hz for (±)-**29** and of 2.2 Hz for (±)-**31** were observed that are typical for the pseudoaxial proton at C(5). The H–C(5) signal of (±)-**29** ($\delta$(H) 4.93) is a broad *s*, therefore showing that $^3J(5,6)$ is smaller than 1.5 Hz. In the case of (±)-**31**, $^3J(5,6) = 3.5$ Hz, which cannot be associated with two axial protons, therefore confirming the *cis* relationship between the 5-bromo and 6-hydroxy substituents. Protons H–C(1) and H–C(6) cannot both occupy axial positions as $^3J(1,6) = 3.9$ Hz in (±)-**29** and 2.0 Hz in (±)-**31**. Again, this demonstrates the *cis* relationship between the substituents at C(1) and C(6), what is expected from the mode of formation of (±)-**29** and (±)-**31** (heterolysis of the tertiary-allylic C–O bond). The $^{13}C$-NMR spectra of (±)-**29** and (±)-**31** established that the C=C bond is between C(3) and C(4) (trisubstituted, not disubstituted alkene). Coupling constant $^3J(1,2) = 1.5$ Hz in (±)-**29** and 5.5 Hz in (±)-**31** suggested different deformations of the pseudo-chair conformations between the tripivalate (±)-**29** and the triacetate (±)-**31** (in cyclohexene, only 2 kcal/mol separate the pseudo-chair and boat conformations). But these coupling constants are consistent with their *cis* relationship, as is expected since there is no reason for an epimerization at C(2) or/and C(3) during the acid-induced oxa-ring openings. The *cis* relationship between H–C(1) and H–C(5) was confirmed by the 2D-NOESY data of (±)-**29** and (±)-**31** that showed strong NOEs between these proton pairs. The structures (±)-**29** and (±)-**31** were further confirmed by their derivatization as shown below (*Scheme 6*).

Acetylation of (±)-**32** gave triacetate (±)-**33** which was fully characterized by its spectral data and elemental analysis. Its structure was established unambiguously by X-ray diffraction of a monocrystal (see *Exper. Part*). Alcohol (±)-**32** was oxidized to enone (±)-**34** (*Jones'* reagent, acetone) in 92% yield (*Scheme 3*). Bicyclic products analogous to (±)-**32** were not observed with the tripivalate (±)-**28** treated under similar conditions. Formation of (±)-**29** and (±)-**31** can be interpreted in terms of the generation of allyl-cation intermediate **35A** arising from the heterolysis of the allylic C(6)–O(7) bond of 7-oxabicyclo[2.2.1]hept-2-ene derivatives **28** and **30** under ether-*Lewis* acid complex formation. Carbenium ion **35A** can equilibrate with dialkoxycarbenium ions **35B** and **35C** resulting from the intramolecular quenching of **35A** by the acetoxymethyl group at C(3) and C(2), respectively. If formed, the latter do not lead to other products than (±)-**29** (R = Piv) or (±)-**31** (R = Ac). Intramolecular transfers of bromide anion generate intermediates of type **36** which are then hydrolyzed to (±)-**29** (R = Piv) or (±)-**31** (R = Ac). The reaction **35** $\rightleftharpoons$ **36** might be reversible at 0°, not at

*Scheme 3*

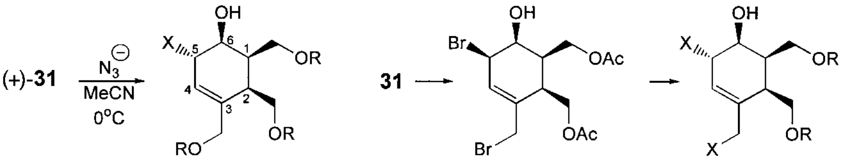


– 78°. If **35A – C** survive long enough, the acetoxymethyl group at C(1) can react with the cationic moiety and generate oxonium ion **37A**, which loses MeCOBr to generate, after aqueous workup, the bicyclic product **32**. Rearrangement **35** → **37** is probably too slow with the tripivalate for steric reasons, thus explaining why the dipivalate analogue of **32** was not observed. The acetoxymethyl groups at C(2) and C(3) of **35** do not participate in the intramolecular quenching of the allyl cationic intermediate, probably because it would lead to more strained bicyclic systems than with the 6-oxabicyclo[3.2.1]oct-3-ene derivative **32**.

The intermediacy of **37A** may appear unlikely since cationic intermediates **35A – C** are expected to be more stable. Since reaction **30** → **32** does not occur below 0°, it implies a free enthalpy of activation of *ca.* 20 kcal/mol. This leaves a significant enthalpy difference between intermediates **37A** and **35A – C** which could be larger than the difference in stability between oxonium ions of type **37A** and the isomeric dialkoxycarbenium ions **35B,C**. Proton affinities (PAs) of ethers and carboxylic esters (PA($Et_2O$) = 198.1 kcal/mol, PA($Me_2O$) = 189.6 kcal/mol, PA(AcOEt) = 195.0 kcal/mol, PA(AcOMe) = 198.1 kcal/mol, PA(HCOOMe) = 188.0 kcal/mol [37]) show that dialkyloxonium ions and alkoxy(hydroxy)carbenium ions of similar size have similar stabilities. High-level quantum calculations [38] reproduce the experimental gas-phase proton affinities with good accuracy. They predict that the difference in enthalpy between the alkoxy-protonated form (acyl-oxonium ion) and the isomeric carbonyl-protonated form (alkoxy(hydroxy)carbenium ion) of an ester or a lactone [39] is only 15 kcal/mol in favor of the carbonyl-protonated form. This enthalpy difference could be even smaller for alkoxy-alkylated *vs.* carbonyl-alkylated esters in solution. The calculations suggest also for $\gamma$-butyrolactone that its alkoxy-protonated form undergoes a facile C–O cleavage with formation of the corresponding $\gamma$-hydroxyacyl cation [39a] [40]. This leaves open the hypothesis that **35A–C** could undergo a two-step (*via* **37A**) or a concerted fragmentation to **37B** + $CH_3CO^+$ (*Scheme 3*). Alternatively, intermediates **35A–C** could undergo intramolecular bromide-anion transfer from the tribromoborate moiety to the vicinal acetoxymethyl group at C(1) with formation of zwitterion **37C**. For steric reasons, this reaction is too slow in the case of the tripivalate **28**. Then **37C** undergoes direct cyclization to generate **32** and MeCOBr, or equilibrates with the dibromoborate **37D** with elimination of MeCOBr. Intermediate **37D** could then cyclize into the dibromoborate of **32** with liberates **32** under aqueous workup.

Displacement of allylic bromide (±)-**31** with tetramethylguanidinium azide [41] occurred in MeCN without allylic rearrangement and with complete inversion of configuration ($S_N2$ rather than $S_N1$ or $S_N2'$) giving azide (±)-**38** in 93% yield (*Scheme 4*). Ammonolysis provided tetrol (±)-**39** (85%), the azido moiety of which could be reduced with $Na_2S \cdot H_2O/Et_3N$ in MeOH [42]. The crude conduramine (±)-**40** was purified by column chromatography (*Dowex 50WX8 H*$^+$; 80–95% yield). Alternatively, catalytic (10% Pd/C) hydrogenation of (±)-**39** led to pure (±)-**40** (97%) fully characterized as its benzyl carbamate (±)-**41**. Starting with enantiomerically pure triacetate (+)-**31**, enantiomerically pure (+)-**38**, (+)-**39**, and (+)-**40** were obtained with similar ease. The *trans* relationship between the 5-azido and 6-hydroxy substituents in (±)-**38** was established by analysis of the product of double-bond *cis*-hydroxylation (±)-**49** (see below, *Scheme 5*). The $^1$H-NMR spectra of **38–41** showed coupling constants $^3J(4,5)$ and $^3J(5,6)$ that vary as a function of the nature of the substituents, suggesting various conformer equilibria for these compounds (H-bridging effect?; presence of boat conformations?).

*Scheme 4*



(+)-**38** R = Ac, X = $N_3$
(+)-**39** R = H, X = $N_3$
(+)-**40** R = H, X = $NH_2$
**41** R = H, X = $NHCO_2Bn$

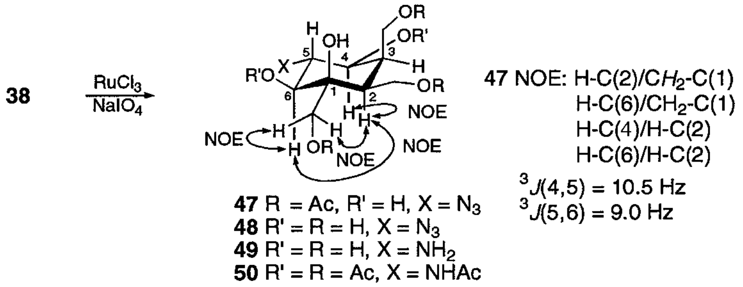
**42**

**43** R = Ac, X = $N_3$
**44** R = H, X = $N_3$
**45** R = H, X = $NH_2$
**46** R = H, X = $NHCO_2Bn$

The treatment of (±)-**31** with $BBr_3$ in $CH_2Cl_2$ led to the selective substitution of the allylic acetate to give dibromide (±)-**42** in 98% yield (*Scheme 4*). Double displacement of dibromide (±)-**42** with tetramethylguanidinium azide produced (±)-**43** (80%), the methanolysis of which provided triol (±)-**44** (96%). Catalytic (Pd/C) hydrogenation of (±)-**44** generated the diaminotriol (±)-**45** (85%), characterized as its double benzyl carbamate (±)-**46** (83%).

*5-Amino-1,4,6-trihydroxycyclohexane-1,2,3-trimethanol* (*Amino[tris(hydroxymethyl)]cyclitol*) **49**. Double hydroxylation of the alkene moiety of (±)-**38** with $RuCl_3 \cdot H_2O/NaIO_4$ in $H_2O$ was face-selective and led to a 6.3 : 1 mixture of two isomeric triols from which the major product (±)-**47** could be isolated (37%) (*Scheme 5*). Its $^1H$-NMR spectrum and 2D-NOESY established the structure and the conformation shown ($^3J(5,6) = 9.0$, $^3J(5,4) = 10.5$ Hz, typical for axial/axial vicinal protons; $^3J(2,3) = 5.0$ Hz, $^3J(3,4) = 4.9$ Hz typical for axial/equatorial vicinal proton pairs; NOE: $\delta$(H) 4.27 ($H_a$ of $CH_2-C(1)$)/3.31 (H–C(6)); 3.59 H–C(4)/2.04 (H–C(2)) and 2.04 (H–C(2))/3.90 ($H_b$ of $CH_2-C(1)$)). The structure of (±)-**47** established the *cis* relationship between the 1-(acetoxymethyl), 6-hydroxy, and 5-bromo substituents of (±)-**31** (*Scheme 3*). Deacetylation of (±)-**47** ($NH_3$/MeOH) provided hexol (±)-**48**, the hydrogenation ($H_2$, Pd/C) of which furnished the expected aminohexol (±)-**49** (90%; *Scheme 5*). This aminocyclitol derivative was fully characterized as its *N*-acetyl-polyacetate (±)-**50**.

*Scheme 5*

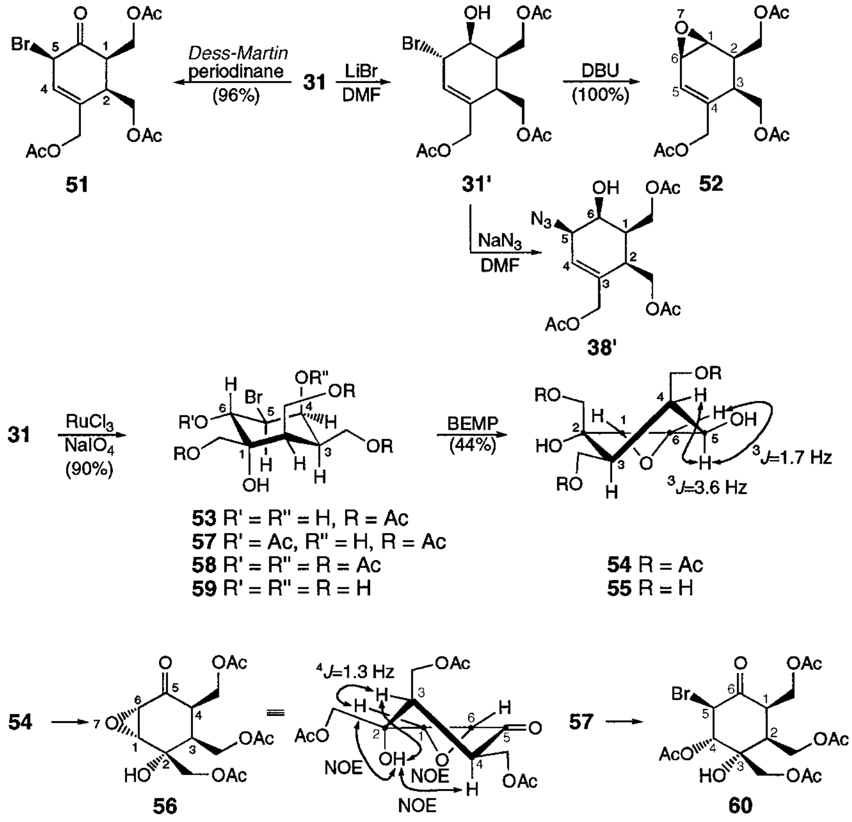


The $^1H$-NMR spectrum of (±)-**50** showed coupling constants $^3J(2,3) = 6.0$ Hz and $^3J(3,4) = 5.5$ Hz typical for equatorial/axial vicinal proton pairs on one hand, and $^3J(4,5) = 11.0$ Hz and $^3J(5,6) = 10.6$ Hz typical for axial/axial vicinal proton pairs on the other hand. The relative configuration of the quaternary center C(1) was given by the mode of formation of (±)-**50** and confirmed by its 2D-NOESY data, which showed strong NOEs between $CH_2-C(1)$ ($\delta$(H) 3.97, 3.93) and H–C(2) ($\delta$(H) 2.27 and H–C(6) ($\delta$(H) 4.88 ppm).

*Epoxides* **55** *and* **67** *of Tris(hydroxymethyl)conduritol and -conduramine, Respectively. Dess-Martin* periodinane oxidation of alcohol (±)-**31** gave enone (±)-**51** (96%) (*Scheme 6*). Elimination of HBr from (±)-**31** on treatment with DBU provided epoxide (±)-**52** in low yield. However, treatment of (±)-**31** with 1.5 equiv. of LiBr in DMF (20°, 2 h) generated the epimeric bromide (±)-**31'** (95%) which eliminated HBr on treatment with DBU, giving (±)-**52** quantitatively. Reaction of (±)-**31'** with $NaN_3$ provided azide (±)-**38'**, the 5-epimer of azide (±)-**38**, which constitutes another confirmation of the structure proposed above for the latter.

The 2D-NOESY data of enone (±)-**51** showed a NOE between H–C(5) ($\delta$(H) 5.18) and H–C(1) ($\delta$(H) 3.25), thus establishing that the 5-bromo-6-oxocyclohex-3-ene moiety has not been epimerized under the oxidation conditions. The structure of (±)-**52** was confirmed by its $^1H$-NMR spectrum which showed $^3J(5,6) = 4.2$ Hz (bond angle expected to be *ca.* 20°), $^4J(3,5) = 1.4$ Hz, $^3J(2,3) = 7.0$ Hz (quasi-eclipsed *cis* C–H bonds), $^3J(1,2) = 2.0$ Hz (bond angle of *ca.* 70°), and $^3J(1,6) = 4.2$ Hz. Furthermore, a NOE was detected between H–C(6) ($\delta$(H) 3.39) and H–C(3) ($\delta$(H) 2.62) on one hand, and between H–C(6) ($\delta$(H) 3.39) and H–C(2) ($\delta$(H) 2.27) on the other hand. The structure of (±)-**38'** was given by its $^1H$-NMR spectrum and its 2D-NOESY data that showed an NOE between H–C(5) ($\delta$(H) 4.00) and H–C(1) ($\delta$(H) 2.21).

*Scheme 6*



Double hydroxylation of allyl bromide (±)-**31** ($RuCl_3/NaIO_4$) was highly face selective, the sterically less-hindered face of the alkene reacting to give triol (±)-**53** in 90% yield. The structure and conformation of (±)-**53** was given by its $^1$H-NMR spectrum and confirmed that of (±)-**31** (*cis* relationship between 5-bromo and 6-hydroxy substituent, see *Scheme 3*).

The $^1$H-NMR spectrum of (±)-**53** showed typical coupling constants between vicinal pairs: $^3J$(2eq, 3ax) 4.5 Hz, $^3J$(3ax,4eq) < 2 Hz, $^3J$(4eq,5ax) = 2.9 Hz, and $^3J$(5ax,6ax) = 10.2 Hz. Coupling constants $^3J$(4,OH) = $^3J$(6,OH) = 4.5 Hz were also observed; they vanished on adding $D_2O$. The relative configuration of the quaternary center C(1) was given by the 2D-NOESY data that showed NOE between H–C(6) ($\delta$(H) 4.02) and one of the protons of the $CH_2$–C(1) group ($\delta$(H) 4.47) on one hand, and between OH–C(1) ($\delta$(H) 2.89, *s*) and H–C(5) ($\delta$(H) 4.39, *dd*) on the other hand.

Treatment of (±)-**53** with BEMP on resin (2-[(*tert*-butyl)imino]-2-(diethylamino)-1,3-dimethylperhydro-1,3,2-diazaphosphorine) at 40° for 2 days generated a major epoxide (±)-**54** isolated in low yield (44%) due to its instability. As expected, elimination of HBr from the *trans*-bromohydrine moiety at C(5), C(6) was favored over that from the *cis*-bromohydrine moiety at C(5), C(4). Methanolysis of (±)-**54** gave the unprotected epoxy pentol (±)-**55**, an unstable compound that underwent polymerization in the condensed state. *Dess-Martin* periodinane oxidation [43] of epoxy diol (±)-**54** produced $\gamma$-hydroxy ketone (±)-**56**. The structure of (±)-**56** confirmed those proposed for (±)-**54** and (±)-**55**.

The $^1$H-NMR spectra of (±)-**54** and (±)-**55** were consistent with the conformation shown in *Scheme 6* for these compounds as $^3J(5,6) = 1.5$ Hz for (±)-**54** and 1.7 Hz for (±)-**55**. The epoxide moiety resides on centers C(1) and C(6) because H–C(1) ($\delta$(H) 3.23 for (±)-**54**, 3.09 for (±)-**55**) couples with H–C(6) ($\delta$(H) 3.49 for (±)-**54**, 3.22 ppm for (±)-**55**). If the epoxide ring resided on centers C(1) and C(2), only one $^1$H signal would be seen for the epoxide. If it were residing between C(5) and C(6) (atom numbering shown in **54**, *Scheme 6*), both signals attributed to the epoxide protons would be *dd*, which is not the case; H–C(1) shows a *d* ($^3J = 3.4$ Hz for (±)-**54**, 3.6 Hz for (±)-**55**) and H–C(6) a *dd*. The chemical shifts observed for H–C(1) and H–C(6) in the $^1$H-NMR spectra of (±)-**54** and (±)-**55** are consistent only with an epoxide, not with an oxetane or tetrahydrofuran ring. The 2D-NOESY data of (±)-**56** showed NOEs between OH–C(2) ($\delta$(H) 3.21) and H–C(3) ($\delta$(H) 2.53) and H–C(4) ($\delta$(H) 3.47) on one hand, and between H–C(1) ($\delta$(H) 3.56) and $CH_2$–C(2) ($\delta$(H) 4.28 and 4.38) on the other hand. The coupling constants $^4J(1,3) = 1.3$ Hz and $^3J(3,4) = 5.0$ Hz are consistent with the near-sofa conformation shown (*Scheme 6*).

Selective acetylation of triol (±)-**53** ($Ac_2O$, pyridine) gave successively tetraacetate (±)-**57** (100%) and pentaacetate (±)-**58** (100%). Methanolysis (MeOH, $NH_3$) of (±)-**53** provided bromo hexol (±)-**59** (86%). *Dess-Martin* periodinane oxidation [43] of (±)-**57** gave (±)-**60**, confirming the structure of **57** (tertiary alcohol, secondary acetate).

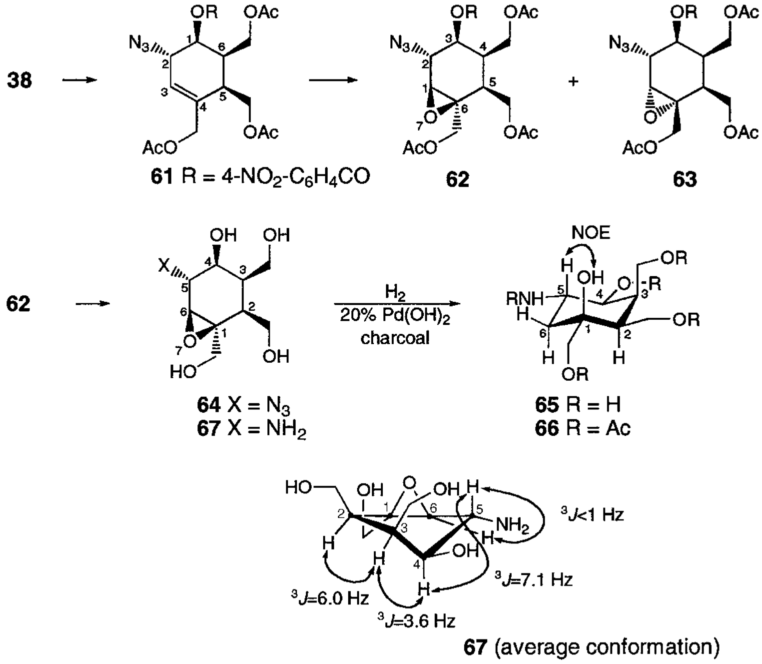
The $^1$H-NMR spectrum of (±)-**59** was similar to that of (±)-**53**, in agreement with the structure and conformation proposed (*Scheme 6*). Typical $^1$H-NMR data of (±)-**60** were: $^3J$(4ax,5ax) = 10.3 Hz, $^3J$(1ax,2eq) = 6.5 Hz; NOE between OH ($\delta$(H) 3.19, *s*) and H–C(2) ($\delta$(H) 4.08) and between H–C(4) ($\delta$(H) 5.63) one H of $CH_2$–C(3) ($\delta$(H) 4.33, *d*, $^2J = 12.5$ Hz).

Esterification of (±)-**38** with 4-nitrobenzoyl chloride ($CH_2Cl_2$, pyridine) afforded (±)-**61** (100%) which was epoxidized with 3-chloroperbenzoic acid (*m*CPBA; 40°, $CH_2Cl_2$) leading to a 3.6:1 mixture of two epoxides. Low-temperature column chromatography (10°, silica gel) permitted isolation of the major isomer (±)-**62** in 46% yield, together with the minor isomer (±)-**63** (2%) and a mixture (±)-**62**/(±)-**63** (26%). Ammonolysis of (±)-**62** (*Scheme 7*) furnished tetrol (±)-**64** (84%), and hydrogenation ($H_2$, 20% $Pd(OH)_2$ on charcoal, 12 h) provided the amino pentol (±)-**65** (90%), which was fully characterized as its *N*-acetyl-peracetate (±)-**66**.

The structure of (±)-**65** was given by its $^1$H-NMR spectrum (in $D_2O$) that showed typical coupling constants $^3J$(2ax,3eq) = 5.4 Hz, $^3J$(3eq,4ax) = 5.4 Hz, $^3J$(4ax,5ax) = 10.4 Hz, $^3J$(5ax,6ax) = 13.0 Hz, and $^3J$(5ax,6eq) = 3.7 Hz. The relative configuration of the quaternary center C(1) was established by the NOEs between one H of $CH_2$–C(1) ($\delta$(H) 3.44, *d*, $^2J = 11.6$ Hz) and H–C(2) ($\delta$(H) 1.95), on one hand, and between the other H of $CH_2$–C(1) ($\delta$(H) 3.37, *d*, $^2J = 11.6$ Hz) and $H_{eq}$–C(6) and ($\delta$(H) 1.84, *dd*, $^2J = 13.0$ Hz, $^3J = 3.7$ Hz), on the other hand. Similar data were collected for (±)-**66**, its 2D-NOESY data ($CDCl_3$) showing a NOE between OH–C(1) ($\delta$(H) 3.50, *s*) and H–C(5) ($\delta$(H) 4.40, *dddd*). The relative configuration of epoxides (±)-**62** and (±)-**63** was confirmed by the observation of coupling constants $^3J(1,2) < 1$ Hz (see sofa conformation of **67**) for (±)-**62** ('*anti*' relationship between the epoxide and azido moieties) and $^3J(1,2) = 3.1$ Hz for (±)-**63**.

When the hydrogenation catalyst was 10% Pd on charcoal (15 min) instead of $Pd(OH)_2$ on charcoal, the epoxide moiety of (±)-**64** was not reduced, and the amino-epoxide (±)-**67** was obtained in 98% yield. The structure of (±)-**67** was deduced from its mode of formation and from its spectral data.

*Scheme 7*



An NOE was observed between H–C(6) (δ(H) 2.98) and H–C(2) (δ(H) 2.52) in the 2D-NOESY of (±)-**67**. The coupling constants $^3J(2,3) = 6.0$ Hz, $^3J(3,4) = 3.6$ Hz, $^3J$(4pseudoax, 5pseudoax) = 7.1 Hz, and $^3J(5,6) <$ 1 Hz measured for (±)-**67** are consistent with the average conformation shown in *Scheme 7* for this compound. Similar coupling constants were measured in the $^1$H-NMR spectra of (±)-**62** and (±)-**64**.

**Enzymatic Assays.** – Compounds (±)-**23**, (±)-**40**, (+)-**40**, (±)-**45**, (±)-**49**, (±)-**59**, (±)-**65**, and (±)-**67** were tested for their inhibitory activity toward a α-L-fucosidase (from bovine placenta), toward three α-D-galactosidases (from coffee bean, *Aspergillus niger*, *Escherichia coli*), five β-D-galactosidases (from *E. coli*, bovine liver, *Aspergillus niger*, *Aspergillus orizae*, jack bean), two maltases (α-glucosidases from yeast, rice), one isomaltase (α-glucosidase from baker's yeast), two amyloglucosidases (from *Aspergillus niger*, *Rhizopus* mold), two β-glucosidases (from almond, *Caldocellum saccharolyticum*, two α-mannosidases (from jack bean, almond), one β-mannosidase (from *Helix pomatia*), one β-xylosidase (from *Aspergillus niger*), one α-*N*-acetylgalactosaminidase (from chicken liver), and three β-*N*-acetylglucosaminidases (from jack bean, bovine epididymis A and B). At 1 mM concentration of the potential inhibitor, 29, 30, and 31% inhibition of β-galactosidase from bovine liver was evaluated for (±)-**40**, (±)-**65**, and (±)-**67**, respectively. No inhibitory activity was found for the other enzymes with the other polyols (±)-**23**, (±)-**45**, (±)-**49**, and (±)-**59**. At 1 mM, enantiomerically pure conduramine analogue (+)-**40** showed 34% inhibition of β-galactosidase from bovine liver, suggesting that (+)-**40** is more active than enantiomer (−)-**40**.

**Conclusion.** – Simple and stereoselective methods were found to convert the *Diels-Alder* adducts of maleic anhydride to furfuryl camphanates into a variety of polyfunctional tris(hydroxymethyl)cyclohexane derivatives including conduritol, conduramine analogues, and their epoxides. All the new polyols and amino polyols presented in this report can be prepared enantiomerically pure in both their enantiomeric forms. They constitute new classes of cyclitol and aminocyclitol derivatives. For the moment, their inhibitory activities toward commercially available glycohydrolases are either nonexistent or weak toward $\beta$-galactosidase from bovine liver (only in the case of (+)-**40**, (±)-**65**, and (±)-**67**).

We are grateful to the *Swiss National Science Foundation*, the *Fonds Herbette*, Lausanne, and the *Stipendienfonds der Basler Chemischen Industrie* for financial support. We thank Mr. *Raynald Demange* for measuring the inhibitory activities reported in this work.

## Experimental Part

*General.* See [44]. Abbreviations: DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DMAP, 4-(dimethylamino)-pyridine; NMO, *N*-methylmorpholine *N*-oxide; PET, light petroleum ether; FC, flash chromatography; CC, column chromatography; Piv, pivaloyl (= 2,2-dimethylpropanoyl)3)). TLC: *Merck* silica gel $60F_{254}$ plates. All the $^1$H-NMR signal assignments were confirmed by 2D-$^1$H-NMR spectroscopy (COSY, NOESY).

*Enzymatic Assays.* Appropriate 4-nitrophenyl glycosides buffered to optimum pH of the enzymes were used; for details, see [45].

5-exo,6-exo-*Dihydroxy-7-oxabicyclo[2.2.1]heptane-1,2*-exo,3-exo-*trimethanol* ((±)-**16**). To a soln. of (±)-**15** (1 g, 5.35 mmol) [33] in MeOH (20 ml) and $H_2O$ (2 ml). NMO (1 g, 8.03 mmol), 750 µl of $OsO_4$ (0.07M in $CCl_4$) were added. The soln. was stirred at 40° under Ar for two days and then evaporated. The residue was dried under high vacuum. An anal. sample was obtained by FC (silica gel; AcOEt/MeOH 8 : 1) 943 mg (80%) of (±)-**16**. White solid, very hygroscopic. M.p. > 255°. $R_f$ (AcOEt/MeOH 8 : 1) 0.05. IR (KBr): 3280, 2995, 2955, 2925, 2885, 1720, 1485, 1375, 1345, 1255, 1130, 1050, 1035, 975, 945, 865, 835, 735, 700, 635, 585. $^1$H-NMR (250 MHz, $CD_3OD$): 4.07 (*s*, H−C(4)); 3.99, 3.76 (2*d*, $^2J = 11.0$, $CH_2$−C(1)); 3.88, 3.83 (2*d*, $^3J = 6.2$, H−C(5), H−C(6)); 3.68, 3.38 (2*dd*, $^2J = 10.5$, $^3J = 4.0$, 8.5, $CH_2$); 3.64, 3.58 (2*dd*, $^2J = 11.0$, $^3J = 6.0$, $CH_2$); 2.08–1.97 (*m*, H−C(2), H−C(3)). $^{13}$C-NMR (100.6 MHz, $CD_3OD$): 89.6 (*m*, C(1)); 84.6 (*d*, $J = 158$, C(4)); 74.8, 74.3 (2*d*, $J = 153$, C(5), C(6)); 60.3, 58.9, 58.2 (3*t*, $J = 140$, $CH_2$); 45.3, 44.9 (2*d*, $J = 132$, C(2), C(3)). CI-MS ($NH_3$): 81 (83), 95 (61), 111 (100), 125 (47), 153 (29), 167 (36), 185 (25), 203 (6), 221 (33).

5-exo,6-exo-*Diacetoxy-7-oxabicyclo[2.2.1]heptane-1,2*-exo-3-exo-*trimethyl Triacetate* ((±)-**17**). A mixture of (±)-**16** (0.5 g, 2.3 mmol), $Ac_2O$ (2 ml), pyridine (2 ml), and DMAP (10 mg) was stirred at 20° for 1 d. Toluene (10 ml) was added, and the solvents were evaporated. This was repeated twice. The residue was purified by FC (silica gel; AcOEt/PET 2.1): 790 mg (80%) of (±)-**17**. White solid. M.p. 116–117°. $R_f$ (AcOEt/PET 2 : 1) 0.44. IR ($CH_2Cl_2$): 3625, 3635, 3100, 3080, 3000, 2950, 2670, 1740, 1730, 1360, 1200, 1110, 1060, 1030, 975, 925, 880. $^1$H-NMR (250 MHz, $CDCl_3$): 5.14, 4.97 (2*d*, $^3J = 6.0$, H−C(5), H−C(6)); 4.40 (*s*, H−C(4)); 4.61, 4.19 (2*d*, $^2J = 12.0$, $CH_2$−C(1)); 4.30 (*dd*, $^2J = 11.5$, $^3J = 2.5$, 1 H); 4.26 (*dd*, $^2J = 11.0$, $^3J = 6.0$, 1 H, $CH_2$); 4.03 (*dd*, $^2J = 11.5$, $^3J = 7.0$, 1 H); 3.95 (*dd*, $^2J = 11.0$, $^3J = 10.0$, 1 H, $CH_2$); 2.35–2.39 (*m*, H−C(2), H−C(3)); 2.02, 2.03, 2.04, 2.06, 2.07 (5*s*, 5 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.6, 170.4, 170.0, 169.9, 169.3 (5*m*, C=O); 86.0 (*s*, C(1)); 81.8 (*d*, $J = 163$, C(4)); 75.1, 74.7 (2*d*, $J = 158$, C(5), C(6)); 61.6, 60.5, 58.8 (3*t*, $J = 150$, 3 $CH_2$); 41.7, 41.1 (2*d*, $J = 136$, C(2), C(3)); 20.9, 20.6, 20.6, 20.5, 20.2, (5*q*, $J = 130$, 5 Me). CI-MS ($NH_3$); 107 (3), 148 (5), 208 (7), 250 (4), 310 (1), 371 (6), 390 (1), 448 (100). Anal. calc. for $C_{19}H_{26}O_{11}$ (430.41): C 53.02, H 6.09; found: C 53.05, H 6.04.

5-exo-6-exo-*Bis(pivaloyloxy)-7-oxabicyclo[2.2.1]heptane-1,2*-exo,3-exo-*trimethyl Tripivalate* ((±)-**18**). A mixture of (±)-**16** (68 mg, 0.312 mmol), dry pyridine (1 ml), and pivaloyl chloride3)) (PivCl; 0.5 ml) was stirred at 20° for 15 h. The excess of PivCl was hydrolyzed by addition of ice, and the solvents were evaporated with toluene (6 ml, 3 times). The residue was taken in $CH_2Cl_2$ (150 ml), washed with aq. sat. $NaHCO_3$ soln. (50 ml)

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3) For convenience, pivaloyl (= 2,2-dimethylpropanoyl) and pivalate (= 2,2-dimethylpropanoate) were also used in systematic names.

and $H_2O$ (30 ml), dried ($MgSO_4$), and evaporated. Crystallization ($Et_2O$/PET) gave 150 mg (80%) of (±)-**18**. White solid. M.p. 157.5 – 159°. $R_f$ ($Et_2O$/PET 1 : 2) 0.28. IR ($CH_2Cl_2$): 3680, 2925, 2885, 1710, 1690, 1670, 1600, 1120, 1065, 1030, 920, 980. $^1$H-NMR (250 MHz, $CDCl_3$): 5.06, 4.92 (2*d*, $^3J=6.4$, H–C(5), H–C(6)); 4.56, 4.29 (2*d*, $^2J=12.0$, $CH_2$–C(1)); 4.33 (*s*, H–C(4)); 4.42 (*dd*, $^2J=11.3$, $^3J=4.1$, 1 H); 4.38 (*dd*, $^2J=11.3$, $^3J=4.5$, 1 H); 4.02, 3.94 (2*d*, $^2J=10.1$, $CH_2$); 3.34, 2.45 (2*dd*, $^3J=8.0$, 4.1, 8.0, 4.5, H–C(2), H–C(3)); 1.23, 1.21, 1.20, 1.18 (4*s*, 45 H, 5 *t*-Bu). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 177 – 178 (5*s*, C=O); 86.1 (*s*, C(1)); 83.0 (*d*, $J=164$, C(4)); 75.6, 75.4 (2*d*, $J=157$, 159, C(5), C(6)); 61.9, 60.9, 59.1 (3*t*, $J=150$, 3 $CH_2$); 42.0, 41.5 (2*d*, $J=132$, 136, C(2), C(3)); 38.8 (*s*); 27.1 – 27.3 (5*q*, $J=128$, 5 *t*-Bu). CI-MS ($NH_3$): 85 (93), 148 (38), 250 (37), 334 (100), 539 (43), 423 (42), 597 (1), 641 (51). Anal. calc. for $C_{34}H_{56}O_{11}$ (640.82): C 63.73, H 8.81; found: C 63.55, H 8.77.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*RS*,6*RS*)-1,4-Dihydroxy-5,6-bis(pivaloyloxy)cyclohexane-1,2,3-trimethyl Tripivalate* ((±)-**19**). $BBr_3$ (80 µl, 0.82 mmol) was added slowly to a stirred soln. of (±)-**18** (350 mg, 0.548 mmol) in anh. $CH_2Cl_2$ (5 ml) under Ar and cooled to 0°. After 10 min at 0°, aq. sat. $NaHCO_3$ soln. (20 ml) was added and the soln. extracted with $CH_2Cl_2$ (150 ml). The org. phase was washed with $H_2O$ (50 ml), dried ($MgSO_4$), and evaporated. FC (silica gel; PET/$Et_2O$ 2 : 1) gave 308 mg (88%) of (±)-**19**. White solid (PET/$Et_2O$). M.p. 161 – 162°. $R_f$ ($Et_2O$/PET 1 : 2) 0.14. UV (MeCN): 205 (3360), 200 (3729). IR (KBr): 2960, 2900, 2890, 1725, 1710, 1480, 1390, 1365, 1280, 1150, 1060, 1030, 980, 945, 890, 770. $^1$H-NMR (250 MHz, $CDCl_3$): 5.40 (*d*, $^3J=4$, H–C(6)); 5.29 (*t*, $^3J=4$, H–C(5)); 4.62 (*dd*, $^2J=12.0$, $^3J=8.0$, 1 H); 4.44 – 4.52 (*m*, 2 H); 4.41, 3.95 (2*d*, $^2J=12.0$, $CH_2$–C(1)); 4.27 (*dd*, $^2J=10.0$, $^3J=7.0$, 1 H, $CH_2$–(3)); 4.00 (br. *d*, $^3J=4.0$, H–C(4)); 2.79 (*s*, OH–C(1)); 2.74, 2.21 (2*m*, H–C(2), H–C(3)); 1.97 (br. *s*, OH–C(4)); 1.22, 1.21, 1.20, 11.9 (5*s*, 45 H, 5 *t*-Bu). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 178.4, 178.3, 178.1, 176.2 (4*s*, C=O); 74.7 (*s*, C(1)); 70.1, 67.6 (2*d*, $J=145$, 146, C(5), C(6)); 69.1 (*d*, $J=154$, C(4)); 67.0 (*t*, $J=150$); 61.9, 62.7 (2*td*, $J=150$, 5, 2 $CH_2$); 38.6 – 38.9 (5*s*); 41.7, 37.0 (2*d*, $J=134$, 126, C(2), C(3)); 26.9 – 27.2 (5*q*, $J=128$, 5 Piv). CI-MS ($NH_3$): 85 (45), 120 (59), 148 (14), 232 (36), 250 (63), 284 (13), 334 (100), 335 (92), 352 (13), 455 (13), 539 (16), 557 (17). Electrospray-MS: 99 (3), 149 (5), 256 (6). Anal. calc. for $C_{34}H_{58}O_{12}$ (658.79): C 62.00, H 8.87; found: C 62.12, H 8.80.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*RS*,6*RS*)-1,4-Bis(methoxymethoxy)-5,6-bis(pivaloyloxy)cyclohexane-1,2,3-trimethyl Tripivalate* ((±)-**20**). An excess of $P_2O_5$ was added in one portion to a stirred mixture of (±)-**19** (90 mg, 0.137 mmol), $CH_2Cl_2$ (1.5 ml), and $(MeO)_2CH_2$ (1.5 ml). The suspension was vigorously stirred for 5 min. It was then filtered and washed with $CH_2Cl_2$. The filtrate was diluted with $CH_2Cl_2$ (150 ml), washed with aq. sat. $NaHCO_3$ soln. (40 ml), dried ($MgSO_4$), and evaporated. Crystallization ($Et_2O$/PET) gave 100 mg (97%) of (±)-**20**. White solid. M.p. 94.5 – 96°. $R_f$ ($Et_2O$/PET 1 : 2) 0.35. IR (KBr): 2975, 2365, 1735, 1480, 1400, 1370, 1285, 1150, 1035, 925, 880, 825, 770, 655, 590, 435. $^1$H-NMR (250 MHz, $CDCl_3$): 5.52 (*d*, $^3J=3.6$, H–C(6)); 5.27 (*t*, $^3J=3.6$, H–C(5)); 4.90, 4.73 (2*d*, $^2J=7$, 6, $OCH_2O$); 4.68, 4.58 (2*d*, $^2J=6.5$, $OCH_2O$); 4.54 – 4.49 (*m*, $CH_2$–C(3)); 4.39 – 4.20 (*m*, $CH_2$–(2), $CH_2$–C(1)); 4.04 (br. *d*, $^3J=3.6$, H–C(4)); 3.42, 3.36 (2*s*, MeO); 2.72, 2.42 (2*m*, H–C(2), H–C(3)); 1.24, 1.22, 1.20, 1.19, 1.18 (5*s*, 5 Piv). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 182 (*m*, C=O); 98.3, 91.7 (2*t*, $J=147$, $OCH_2O$); 80.1 (br. *s*, C(1)); 73.9, 71.2 (2*d*, $J=145$, C(5), C(6)); 68.5 (*d*, $J=154$, C(4)); 63.3, 62.8, 62.1 (3*t*, $J=156$, 3 $CH_2$); 56.7, 56.4 (*q*, $J=128$, 2 MeO); 39.6, 36.9 (2*d*, $J=134$, 124, C(2), C(3)); 38.9 (br. *s*); 27.1 – 27.4 (5*q*, $J=127$, 5 *t*-Bu). CI-MS ($NH_3$): 85 (7), 148 (1), 249 (2), 383 (3), 467 (7), 539 (9), 569 (26), 641 (25), 658 (35), 686 (8). Anal. calc. for $C_{38}H_{66}O_{14}$ (746.94): C 61.11, H 8.91; found: C 61.21, H 8.93.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*RS*,6*RS*)-1,4-Diacetoxy-5,6-bis(pivaloyloxy)cyclohexane-1,2,3-trimethyl Tripivalate* ((±)-**21**). A mixture of (±)-**19** (9 mg, 0.014 mmol), $CH_2Cl_2$ (0.5 ml), pyridine (0.5 ml), $Ac_2O$ (0.5 ml), and DMAP (1 mg) was stirred at 20° for 15 h. The solvents were evaporated with toluene (5 ml, 3 times), and the residue was purified by FC (silica gel; PET/$Et_2O$ 3 : 1): 10 mg (100%) of (±)-**21**. White solid. M.p. 177 – 178°. $R_f$ ($Et_2O$/PET 1 : 2) 0.40. IR ($CH_2Cl_2$): 2975, 2935, 2910, 2875, 1740, 1480, 1460, 1400, 1365, 1280, 1225, 1185, 1150, 1055. $^1$H-NMR (250 MHz, $CDCl_3$): 5.55 (*d*, $^3J=4.1$, H–C(6)); 5.50 (br. *d*, $^3J=4.1$, H–C(4)); 5.30 (*t*, $^3J=4.1$, H–C(5)); 4.90, 4.40 (2*d*, $^2J=12.6$, $CH_2$–C(1)); 4.61 (*dd*, $^2J=12.3$, $^3J=8.8$, 1 H), 4.44 (*dd*, $^2J=12.3$, $^3J=3.9$, 1 H, $CH_2$–C(2)); 4.25 (*dd*, $^2J=11.2$, $^3J=8.4$, 1 H), 3.98 (*dd*, $^2J=11.2$, $^3J=7.7$, 1 H, $CH_2$–C(3)); 3.33 (br. *m*, $^3J=8.4$, 7.7, H–C(3)); 2.63 (br. *m*, $^3J=8.8$, 3.9, H–C(2)); 2.12, 2.09 (2*s*, 2 Ac); 1.25, 1.23, 1.20, 1.19, 1.12 (5*s*, 5 Piv). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 175.9 – 179.0 (5*s*, C=O (Piv)); 169.5, 168.8 (2*s*, C=O (Ac)); 84.1 (*s*, C(1)); 67.6 (*dt*, $J=142$, 4, C(5)); 66.8 (*dd*, $J=156$, 6, C(4)); 66.5 (*d*, $J=147$, C(6)); 61.5 (*t*, $J=158$, $CH_2$–C(1)); 60.9, 60.8 (2*t*, $J=148$, 2 $CH_2$); 38.8 (*s*); 38.7, 35.6 (2*d*, $J=132$, 127, C(2), C(3)); 27.3 – 27.0 (5*q*, $J=122$, 5 *t*-Bu); 22.0, 20.9 (2*q*, $J=130$, 2 Me). CI-MS ($NH_3$): 85 (100), 148 (13), 232 (37), 292 (6), 334 (21), 376 (17), 497 (3), 641 (4), 761 (4). Anal. calc. for $C_{38}H_{61}O_{14}$ (741.90): C 61.52, H 8.29; found: C 61.50, H 8.35.

*(1*RS*,2*RS*,3*SR*,5*SR*,6*RS*)-1-Hydroxy-4-oxo-5,6-bis(pivaloyloxy)cyclohexane-1,2,3-trimethyl Tripivalate* ((±)-**22**). At 0° and under stirring, aq. 4N *Jones'* reagent ($CrO_3$, $H_2SO_4$, 0.15 ml) was added to a soln. of (±)-**19** (194 mg, 0.296 mmol) in acetone (5 ml). After 10 min, the suspension was stirred at 20°, and more reagent

(0.05 ml) was added. After 50 min i-PrOH was added slowly until the orange color disappeared. The suspension was filtered over a *Celite* pad. The filtrate was diluted with $CH_2Cl_2$ (200 ml), washed with aq. sat. $NaHCO_3$ soln. (50 ml), dried ($MgSO_4$), and evaporated. Recrystallization (PET/$Et_2O$) gave 192 mg (100%) of (±)-**22**. White solid. M.p. 78–79.5°. $R_f$ ($Et_2O$/PET 1 : 2) 0.35. UV (MeCN): 191 (4900). $^1$H-NMR (250 MHz, $CDCl_3$): 5.78 (*d*, $^3J$ = 4.5, H–C(6)); 5.66 (*dd*, $^3J$ = 4.5, $^4J$(5,3) = 2.0, H–C(5)); 4.61 (*dd*, $^2J$ = 11.5, $^3J$ = 8.0, 1 H); 4.49, 4.08 (2*d*, $^2J$ = 12.0, $CH_2$–C(1)); 4.24 (*dd*, $^2J$ = 12.0, $^3J$ = 4.5, 1 H); 4.10 (*dd*, $^2J$ = 11.5, $^3J$ = 5.0, 1 H, $CH_2$–C(3)); 3.94 (*dd*, $^2J$ = 12.0, $^3J$ = 8.0, 1 H, $CH_2$–C(2)); 3.64 (*s*, OH–C(1)); 2.66, 1.67 (2*m*, H–C(2), H–C(3)); 1.25–1.18 (5*s*, 5 Piv). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 200.2 (*s*, C(4)); 176.1–179.1 (5 br. *s*, C=O); 74.4 (*d*, *J* = 154, C(5)); 73.7 (*dd*, *J* = 148, 5, C(6)); 74.1 (br. *s*, C(1)); 66.3, 61.5, 60.3 (3*t*, *J* = 149, 3 $CH_2$); 47.1, 45.8 (2*d*, *J* = 135, 129, C(2), C(3)); 38.6–39.1 (5 br. *s*); 26.8–27.3 (5*q*, *J* = 129, 5 *t*-Bu). CI-MS ($NH_3$): 85 (97), 151 (100), 235 (66), 248 (25), 337 (22), 350 (22), 350 (17), 501 (8), 539 (3), 674 (3), 435 (15), 452 (21). Anal. calc. for $C_{34}H_{56}O_{12}$ (656.82): C 62.17, H 8.59; found: C 62.21, H 8.64.

*(1*RS*,2*RS*,3*RS*,4*RS*,5*SR*,6*RS*)-1,5,6-Tris(hydroxymethyl)cyclohexane-1,2,3,4-tetrol* ((±)-**23**). A mixture of (±)-**19** (280 mg, 0.425 mmol), anh. MeOH (2 ml), and 5.4M NaOMe in MeOH (0.5 ml) was stirred at 20° for 24 h. The soln. was neutralized with 1N HCl, evaporated, and dried under high vacuum. An anal. sample was obtained by CC (silica gel; AcOEt/MeOH 3 : 2): 62.8 mg (62%) of (±)-**23**. Very hygroscopic white solid. $R_f$ (AcOEt/MeOH 3 : 2) 0.16. $^1$H-NMR (250 MHz, $CD_3OD$): 4.02 (*dd*, $^3J$ = 3.2, 2.4, H–C(4)); 3.93, 3.77 (2*d*, $^2J$ = 11.6, $CH_2$–C(1)); 3.87 (*dd*, $^2J$ = 11.2, 7.9, 1 H); 3.85 (*dd*, $^3J$ = 3.9, 3.2, H–C(3)); 3.82 (*dd*, $^2J$ = 12.0, $^3J$ = 5.0, 1 H); 3.77 (*dd*, $^2J$ = 11.2, $^3J$ = 7.0, 1 H, $CH_2$–C(5)); 3.72 (*dd*, $^2J$ = 12.0, 3.1, 1 H, $CH_2$–C(6)); 3.70 (*d*, $^3J$ = 3.9, H–C(2)); 2.42 (*dtd*, $^3J$ = 7.9, 7.0, 2.4, H–C(5)); 2.08 (*ddd*, $^3J$ = 7.0, 5.0, 3.1, H–C(6)). $^{13}$C-NMR (400 MHz, $D_2O$): 78.9 (*s*, C(1)); 74.6, 71.7, 70.5 (3*d*, *J* = 147, 148, 142, C(2), C(3), C(4)); 67.3 (*t*, *J* = 143, $CH_2$); 63.1 (*td*, *J* = 142, 7, $CH_2$); 59.7 (*tt*, *J* = 144, 5, $CH_2$); 45.2, 42.2 (2*d*, *J* = 125, 124, C(5), C(6)). CI-MS ($NH_3$): 79 (85), 95 (100), 110 (68), 124 (83), 154 (61), 167 (11), 203 (4), 221 (9), 239 (3).

*(1*RS*,2*RS*,3*SR*,4*RS*,5*RS*,6*RS*)-1-Hydroxy-4,5,6-triacetoxycyclohexane-1,2,3-trimethyl Triacetate* ((±)-**24**). The crude reaction residue from the methanolysis of (±)-**19** was acetylated with dry pyridine/$Ac_2O$ 1 : 1 (2 ml) and DMAP (5 mg) for 24 h at 20°. The solvents were evaporated with toluene (5 ml, 3 times), and the residue was purified by FC (silica gel; AcOEt/PET 1 : 2, then 2 : 1): 158 mg (76%) of (±)-**24**. Colorless oil. $R_f$ (AcOEt/PET 2 : 1) 0.48. IR (film): 3470, 2970, 1745, 1730, 1650, 1435, 1370, 1230, 1100, 1045, 970, 735. $^1$H-NMR (400 MHz, $CDCl_3$): 5.45 (*dd*, $^3J$ = 3.9, 2.8, H–C(4)); 5.35 (*t*, $^3J$ = 3.9, H–C(3)); 5.26 (*d*, $^3J$ = 3.9, H–C(2)); 4.54 (*dd*, $^2J$ = 12.4, $^3J$ = 7.6, 1 H); 4.48, 3.98 (2*d*, $^2J$ = 11.9, $CH_2$–C(1)); 4.38 (*dd*, $^2J$ = 12.4, $^3J$ = 4.9, 1 H, $CH_2$–C(6)); 4.17 (*dd*, $^2J$ = 11.1, $^3J$ = 9.3, 1 H); 4.11 (*dd*, $^2J$ = 11.1, $^3J$ = 5.4, 1 H, $CH_2$–C(5)); 3.12 (*s*, OH–C(1)); 2.86 (*dddd*, $^3J$ = 9.3, 5.4, 5.0, 2.8, H–C(5)); 2.24 (*ddd*, $^3J$ = 7.6, 4.9, 5.0, H–C(6)); 2.10, 2.09, 2.08, 2.05, 2.04, 1.94 (6*s*, 6 Ac). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.8, 169.2 (6*s*, C=O); 73.9 (*s*, C(1)); 69.2, 67.9, 67.4 (3*d*, *J* = 152, 145, 154, C(2), C(3), C(4)); 66.2 (*t*, *J* = 150, *C*$H_2$–C(1)); 62.0, 60.9 (2*t*, *J* = 148, 150, 2 $CH_2$); 41.9, 35.4 (2*d*, *J* = 132, 129, C(6), C(5)); 21.0–20.5 (6*q*, 6 Me). Anal. calc. for $C_{21}H_{30}O_{13}$ (490.46): C 51.43, H 6.17; found: C 51.50, H 6.27.

*7-Oxabicyclo[2.2.1]hept-5-ene-1,2-*exo*,3-*exo*-trimethyl Tripivalate* ((±)-**28**). To a soln. of (±)-**15** (200 mg, 1.074 mmol) [33] in dry pyridine (1 ml) and dry $CH_2Cl_2$ (0.5 ml), PivCl (0.529 ml, 4.296 mmol) was added, and the soln. was stirred at 20° for 15 h. The excess of PivCl was hydrolyzed by addition of ice, and the residue was taken in $CH_2Cl_2$ (150 ml), washed with aq. $NaHCO_3$ soln. (50 ml) and $H_2O$ (30 ml), dried ($MgSO_4$), and evaporated. The excess of pyridine was evaporated with toluene (10 ml). Crystallization ($CH_2Cl_2$/PET) gave 438 mg (93%) of (±)-**28**. White solid. M.p. 63.0–64.5°. $R_f$ (AcOEt/PET 1 : 2) 0.67. UV (MeCN): 192 (7600). IR (KBr): 2970, 2875, 1730, 1480, 1460, 1400, 1365, 1285, 1165, 1120, 1035, 995, 940, 895, 815, 770, 700, 635, 525. $^1$H-NMR (250 MHz, $CDCl_3$): 6.39 (*dd*, $^3J$ = 5.7, 1.4, H–C(5)); 6.25 (*d*, $^3J$ = 5.7, H–C(6)); 4.82 (*d*, $^3J$ = 1.4, H–C(4)); 4.75, 4.35 (2*d*, $^2J$ = 12.4, $CH_2$–C(1)); 4.35 (*dd*, $^2J$ = 11.5, $^3J$ = 5.1, 1 H); 4.30 (*dd*, $^2J$ = 11.5, $^3J$ = 4.8, 1 H, $CH_2$); 4.09 (*dd*, $^2J$ = 12.4, $^3J$ = 7.9, 1 H); 4.01 (*dd*, $^2J$ = 12.4, $^3J$ = 10.4, 1 H, $CH_2$); 2.17–2.11 (br. *m*, $^3J$ = 10.4, 7.9, 5.1, 4.8, H–C(2), H–C(3)); 1.23, 1.21, 1.20 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 177.8 (*m*, C=O); 136.4, 135.9 (2*d*, *J* = 178, C(5), C(6)); 89.2 (*s*, C(1)); 80.2 (*d*, *J* = 161, C(4)); 63.4, 61.9, 61.8 (3*t*, *J* = 150, 3 $CH_2$); 41.4, 40.9 (2*d*, *J* = 137, 139, C(2), C(3)); 38.8 (*s*); 27.1–27.0 (3*q*, 3 *t*-Bu). CI-MS ($NH_3$): 81 (34), 98 (5), 182 (5), 235 (13), 274 (1), 319 (11), 439 (7), 456 (100). Anal. calc. for $C_{24}H_{38}O_7$ (438.60): C 65.75, H 8.76; found: C 65.84, H 8.60.

*(1*RS*,2*RS*,5*RS*,6*SR*)-5-Bromo-6-hydroxycyclohex-3-ene-1,2,3-trimethyl Tripivalate* ((±)-**29**). $BBr_3$ (0.018 ml, 0.20 mmol) was added to a stirred soln. of (±)-**28** (100 mg, 0.228 mmol) in $CH_2Cl_2$ (1 ml) cooled to 0° under Ar. The soln. was stirred at 0° for 5 min. It was then diluted with $CH_2Cl_2$ (100 ml), washed twice with $H_2O$ (20 ml), dried ($MgSO_4$), and evaporated. FC (silica gel; AcOEt/PET 1 : 2) gave 112 mg (95%) of (±)-**29**. M.p. 118–119°. $R_f$ (AcOEt/PET 1 : 2) 0.52. IR (film): 3490, 2970, 1730, 1480, 1400, 1365, 1285, 1230, 1155, 1035, 980,

865. $^1$H-NMR (400 MHz, $CDCl_3$): 5.81 (br. *d*, $^4J = 4.0$, H–C(4)); 4.72, 4.66, 4.63 (3 br. *s*); 4.93 (br. *s*, H–C(5)); 4.55 (*dd*, $^2J = 12.0$, $^3J = 4.1$, 1 H); 4.42 (*dd*, $^2J = 11.2$, $^3J = 8.4$, 1 H); 4.34 (*dd*, $^2J = 11.2$, $^3J = 6.9$, 1 H, $CH_2$–C(1)); 4.18 (*dd*, $^2J = 12.0$, $^3J = 6.6$, 1 H, $CH_2$–C(2)); 4.04 (br. *d*, $^3J = 3.9$, H–C(6)); 2.57 (*m*, $^3J = 6.6$, 4.1, 1.5, H–C(2)); 2.36 (*dddd*, $^3J = 8.4$, 6.9, 3.9, 1.5, H–C(1)); 1.22, 1.21, 1.20 (3*s*, 3 *t*-Bu). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 177.8 (*m*, C=O); 138.0 (*s*, C(3)); 124.1 (*d*, $J = 166$, C(4)); 66.4 (*d*, $J = 153$, C(6)); 65.6, 64.6, 63.4 (3*t*, $J = 152$, 3 $CH_2$); 55.1 (*d*, $J = 154$, C(5)); 40.9 (*d*, $J = 127$, C(2)); 35.5 (*d*, $J = 127$, C(1)); 38.8 (*s*); 27.0–27.2 (*q*, $J = 129$, 3 *t*-Bu). CI-MS ($NH_3$): 79 (11), 81 (5), 85 (100), 104 (36), 105 (32), 120 (42), 121 (23), 133 (94), 205 (19), 235 (15), 319 (5), 439 (4). Anal. calc. for $C_{24}H_{39}BrO_7$ (519.48): C 55.49, H 7.51, Br 15.40; found: C 55.50, H 7.52, Br 15.33.

*7-Oxabicyclo[2.2.1]hept-5-ene-1,2-*exo*,3-*exo*-trimethyl Triacetate* ((–)-**30**). A soln. of (–)-**15** (1 g, 5.37 mmol) [31] in dry $CH_2Cl_2$ (2 ml), dry pyridine (2 ml), and $Ac_2O$ (2 ml) was stirred at 20° until complete protection. Toluene (10 ml) was added, and the solvents were evaporated under reduced pressure at 30°. This was repeated twice. The residue was purified by FC (silica gel; AcOEt/PET 1 : 1): 1.424 g (95%) of (–)-**30**. White solid. M.p. 81–82°. $R_f$ (AcOEt/PET 2 : 1) 0.50. $[\alpha]^{25}_{589} = -7$, $[\alpha]^{25}_{577} = -2$, $[\alpha]^{25}_{546} = -4$, $[\alpha]^{25}_{405} = -6$ ($c = 0.3$, $CHCl_3$). UV (MeCN): 192 (5850). IR (KBr): 2965, 1740, 1370, 1280, 1245, 1120, 1040, 995, 945, 900, 865, 845, 805, 705, 635, 605, 440. $^1$H-NMR (250 MHz, $CDCl_3$): 6.42 (*dd*, $^3J = 5.8$, 1.6, H–C(5)); 6.27 (*d*, $^3J = 5.8$, H–C(6)); 4.82 (*d*, $^3J = 1.6$, H–C(4)); 4.74, 4.33 (2*d*, $^2J = 12.6$, $CH_2$–C(1)); 4.32 (*dd*, $^2J = 12.0$, $^3J = 3.0$, 1 H); 4.25 (*dd*, $^2J = 12.0$, $^3J = 5.0$, 1 H); 4.08 (*dd*, $^2J = 11.5$, $^3J = 8.5$, 1 H), 3.99 (*dd*, $^2J = 11.5$, $^3J = 9.0$, $CH_2$); 2.17–2.12 (br. *m*, $^3J = 9.0$, 8.5, 5.0, 3.0, H–C(2), H–C(3)); 2.09, 2.08, 2.07 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.4, 170.3, 170.0 (3*s*, C=O); 135.8, 135.7 (2*d*, $J = 176$, C(5), C(6)); 88.5 (*s*, C(1)); 80.0 (*d*, $J = 161$, C(4)); 63.1, 61.8, 61.5 (3*t*, $J = 163$, $CH_2$); 41.0, 40.4 (2*d*, $J = 137$, 140, C(2), C(3)); 20.8, 20.5, 20.4 (3*q*, $J = 130$, 3 Me). CI-MS ($NH_3$): 81 (12), 98 (57), 133 (29), 175 (6), 193 (45), 211 (10), 235 (13), 313 (12), 330 (100). Anal. calc. for $C_{15}H_7O_{20}$ (312.32): C 57.69, H 6.41, O 35.90; found: C 57.63, H 6.32, O 35.95.

*(1*R*,2*R*,5*R*,6*S*)-5-Bromo-6-hydroxycyclohex-3-ene-1,2,3-trimethyl Triacetate* ((±)-**31**). $BBr_3$ (0.23 ml, 3.2 mmol) was added dropwise to a stirred soln. of (–)-**30** [31] (0.5 g, 1.603 mmol) in anh. $CH_2Cl_2$ (5 ml) cooled to –78° under Ar. After complete dissolution of $BBr_3$, the soln. was stirred for 15 min. It was then diluted with $CH_2Cl_2$ (500 ml), washed twice with $H_2O$ (100 ml), dried ($MgSO_4$), and evaporated. FC (silica gel; AcOEt/PET 2 : 1) gave 598 mg (95%) of (+)-**31**. Beige, unstable solid (storage in the freezer). M.p. 79–81°. $R_f$ (AcOET/PET 2 : 1) 0.35. $[\alpha]^{25}_{589} = +15$, $[\alpha]^{25}_{577} = +12$, $[\alpha]^{25}_{546} = +13$, $[\alpha]^{25}_{405} = +12$ ($c = 0.37$, $CHCl_3$). IR (KBr): 3440, 2900, 1745, 1720, 1485, 1470, 1365, 1345, 1275, 1240, 1180, 1155, 1100, 1035, 960, 915, 865, 755, 715, 655, 605, 525. $^1$H-NMR (250 MHz, $CDCl_3$): 5.83 (*dq*, $^3J = 2.2$, $^4J = 1.2$, H–C(4)); 4.91 (br. *m*, $^3J = 3.5$, 2.2, H–C(5)); 4.73, 4.57 (2 br. *d*, $^2J = 13.5$, $CH_2$–C(3)); 4.50 (*dd*, $^2J = 11.7$, $^3J = 4.7$, 1 H); 4.38 (*d*, $^3J = 7.4$, $CH_2$–C(1)); 4.21 (*dd*, $^2J = 11.7$, $^3J = 6.8$, 1 H, $CH_2$–C(2)); 4.07 (br. *ddd*, $^3J = 4.2$, 3.5, 2.0, H–C(6)); 2.61 (br. *ddd*, $^3J = 6.8$, 5.5, 4.7, H–C(2)); 2.33 (*tdd*, $^3J = 7.4$, 5.5, 2.0, H–C(1)); 2.48 (*d*, $^3J = 4.2$, OH); 2.10, 2.08, 2.05 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 171.1, 170.8, 170.7 (3*s*, C=O); 137.7 (*s*, C(3)); 125.4 (*dq*, $J = 166$, 5, C(4)); 66.6 (*d*, $J = 147$, C(6)); 66.0 (*t*, $J = 149$, *C*$H_2$–C(3)); 63.7, 63.1 (2*t*, $J = 149$, 2 $CH_2$); 55.0 (*d*, $J = 152$, C(5)); 41.0 (*d*, $J = 128$, C(2)); 35.8 (*d*, $J = 130$, C(1)); 21.3, 21.2, 21.2 (3*q*, $J = 130$, 3 Me). CI-MS ($NH_3$): 79 (10), 81 (5), 91 (34), 104 (25), 105 (26), 107 (159, 120 (34), 121 (27), 132 (20), 133 (100), 134 (27), 151 (16), 163 (31), 193 (38), 211 (12), 275 (12), 273 (9), 313 (6).

*(1*RS*,2*RS*,5*SR*,8*SR*)-2-*endo*-Hydroxy-6-oxabicyclo[3.2.1]oct-3-ene-5,8-dimethyl Diacetate* ((±)-**32**). $BBr_3$ (46 µl, 0.48 mmol) was added to a stirred soln. of (±)-**30** (50 mg, 0.16 mmol) in anh. $CH_2Cl_2$ (4 ml) cooled to –78° under Ar. After stirring at 0° for 20 min, the soln. was diluted with $CH_2Cl_2$ (100 ml), washed with $H_2O$ (20 ml), dried ($MgSO_4$), and evaporated. FC (silica gel; AcOEt/PET 2 : 1) gave 20.1 mg (46%) of (±)-**32** and 29.3 mg (47%) of (±)-**31**. Data of (±)-**32**: colorless oil. $R_f$ (AcOEt/PET 2 : 1) 0.20. IR (film): 3450, 3040, 2955, 2895, 1745, 1430, 1370, 1235, 1115, 1080, 1040, 995, 910, 735. $^1$H-NMR (250 MHz, $CDCl_3$): 5.92 (*dd*, $^3J = 9.6$, $^4J = 2.0$, H–C(4)); 5.76 (*dt*, $^3J = 9.6$, 2.0, $^4J = 2.0$, H–C(3)); 4.67 (br. *t*, $^3J = 2.0$, H–C(2)); 4.29, 4.23 (2*d*, $^2J = 11.5$, $CH_2$–C(5)); 4.15 (*dd*, $^2J = 11.2$, $^3J = 6.5$, 1 H); 4.11 (*dd*, $^2J = 9.0$, $^3J = 4.0$, 1 H); 4.03 (*dd*, $^2J = 11.2$, $^3J = 7.0$, 1 H, $CH_2$–C(8)); 3.95 (*dd*, $^2J = 9.0$, $^3J = 6.0$, 1 H, $CH_2$–C(1)); 2.59 (br. *dd*, $^3J = 6.0$, 4.0, H–C(1)); 2.32 (*dd*, $^3J = 7.0$, 6.5, H–C(8)); 2.11, 2.07 (2*s*, 2 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.9, 170.7 (2*m*, C=O); 131.2, 131.4 (2 br. *d*, $J = 165$, C(3), C(4)); 78.7 (*s*, C(5)); 72.0 (*d*, $J = 144$, C(2)); 64.8, 64.6, 62.6 (3*t*, $J = 147$, 3 $CH_2$); 47.3, 45.1 (2*d*, $J = 140$, C(8), C(1)); 20.8, 20.9 (2*q*, $J = 130$, 2 Me). CI-MS ($NH_3$): 79 (13), 81 (22), 80 (3), 91 (25), 104 (100), 107 (35), 121 (39), 121 (33), 133 (18), 150 (55), 211 (17), 253 (6), 271 (10). Anal. calc. for $C_{13}H_{18}O_6$ (270.28): C 57.77, H 6.71; found: C 57.85, H 6.61.

*(1*RS*,2*RS*,5*SR*,8*SR*)-2-Acetoxy-6-oxabicyclo[3.2.1]oct-3-ene-5,8-dimethyl Diacetate* ((±)-**33**). A mixture of (±)-**32** (20 mg, 0.074 mmol), pyridine (0.5 ml), $Ac_2O$ (0.5 ml), and DMAP (2 mg) was stirred at 20° for 24 h. The solvents were evaporated with toluene (5 ml, 3 times), and the residue was purified by FC (silica gel; AcOEt/PET 1 : 2). Crystallization ($CH_2Cl_2/Et_2O$) gave 23 mg (96%) of (±)-**33**. Colorless crystals. M.p. 89–90°.

$R_f$ (AcOEt/PET 1 : 2) 0.11. IR ($CH_2Cl_2$): 3045, 2950, 2910, 1745, 1650, 1480, 1470, 1390, 1365, 1260, 1185, 1085, 1040, 1025, 985, 895. $^1$H-NMR (250 MHz, $CDCl_3$): 6.01 (*dd*, $^3J=9.6$, $^4J=1.6$, H−C(4)); 5.73 (*ddd*, $^3J=9.6$, 2.0, $^4J=2.0$, H−C(3)); 5.65 (*ddd*, $^3J=4.0$, 2.0, $^4J=1.6$, H−C(2)); 4.28, 4.24 (2*d*, $^2J=11.3$, $CH_2$−C(5)); 4.13 (*dd*, $^2J=11.3$, $^3J=7.7$, 1 H); 4.09 (*dd*, $^2J=9.4$, $^3J=1.1$, $H_a$−C(7)); 3.99 (*dd*, $^2J=11.3$, $^3J=6.9$, 1 H, $CH_2$−C(8)); 3.94 (*dd*, $^2J=9.4$, $^3J=1.6$, $H_b$−C(7)); 2.73 (br. *ddd*, $^3J=4.0$, 1.6, 1.1, H−C(1)); 2.41 (*dd*, $^3J=7.7$, 6.9, H−C(8)); 2.11, 2.08, 2.07 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.7, 170.5, 170.3 (3*m*, C=O); 133.4 (*dd*, $J=164.0$, 4.6, C(4)); 127.7 (*dd*, $J=165.0$, 6.0, C(3)); 78.7 (*s*, C(5)); 74.6 (*d*, $J=155$, C(2)); 65.4, 64.4, 62.2 (3*t*, $J=159$, 149, 147, 3 $CH_2$); 47.4 (*d*, $J=137$, C(1)); 42.3 (*d*, $J=141$, C(8)); 21.1, 20.8, 20.7 (3*q*, $J=130$, 3 Me). CI-MS ($NH_3$): 91 (28), 104 (100), 120 (37), 150 (16), 192 (4), 253 (9). Anal. calc. for $C_{25}H_{20}O_7$ (312.32): C 57.69, H 6.45; found: C 57.42, H 6.64.

For the single-crystal X-ray diffraction of (±)-**33**, see below.

*(1RS,5SR,8SR)-2-Oxo-6-oxabicyclo[3.2.1]oct-3-ene-5,8-dimethyl Diacetate* ((±)-**34**). Aq. 4N *Jones*' reagent ($CrO_3$, $H_2SO_4$, 60 μl) was added to a stirred soln. of (±)-**32** (12 mg, 0.044 mmol) in acetone cooled to 0°. After stirring at 20° for 10 min TLC control (silica gel, AcOEt/PET 2 : 1)), i-PrOH was added dropwise till a green color persisted. The suspension was diluted with $CH_2Cl_2$ (50 ml), filtered, washed with sat. aq. $NaHCO_3$ soln. (10 ml) and $H_2O$ (10 ml), dried ($MgSO_4$), and evaporated to afford 11.9 mg (100%) of (±)-**34**. If necessary, further purification by FC (silica gel; AcOEt/PET 1 : 1) afforded pure (±)-**34** (11 mg, 92%). Colorless oil. $R_f$ (AcOEt/PET 2 : 1) 0.40. IR ($CH_2Cl_2$): 3035, 2955, 2895, 2360, 1740, 1650, 1430, 1370, 1235, 1180, 1115, 1080, 1040, 995, 930, 910, 850, 735, 680. $^1$H-NMR (250 MHz, $CDCl_3$): 7.14 (*d*, $^3J=9.5$, H−C(4)); 6.16 (*dd*, $^3J=9.5$, $^4J=1.5$, H−C(3)); 4.42, 4.32 (2*d*, $^2J=11.0$, $CH_2$−C(5)); 4.29 (*dd*, $^2J=10.0$, $^3J=6.0$, $H_a$−C(7)); 4.13, 3.95 (2*dd*, $^2J=11.0$, $^3J=7.0$, $CH_2$−C(8)); 3.67 (*d*, $^2J=10.0$, $H_b$−C(7)); 3.16 (*dd*, $^3J=6.0$, $^4J=1.5$, H−C(1)); 2.69 (*t*, $^3J=7.0$, H−C(8)); 2.14, 2.08 (2*s*, 2 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 200.0 (*s*, C(2)); 174.0 (*m*, C=O); 151.0 (*d*, $J=165$, C(4)); 129.9 (*d*, $J=168$, C(3)); 77.6 (*s*, C(5)); 65.6 (*t*, $J=150$); 63.8, 63.2 (2*t*, $J=146$, 2 $CH_2$); 53.3 (*d*, $J=145$, C(1)); 49.6 (*d*, $J=140$, C(8)); 20.7 (*q*, $J=133$, 2 Me). CI-MS ($NH_3$): 107 (2), 120 (8), 149 (7), 179 (8), 209 (5), 269 (5), 269 (100), 286 (49). Anal. calc. for $C_{13}H_{16}O_6$ (268.27): C 58.20, H 6.01; found: C 58.06, H 6.03.

*(1R,2R,5S,6S)-5-Azido-6-hydroxycyclohex-3-ene-1,2,3-trimethyl Triacetate* ((±)-**38**). A mixture of (+)-**31** (4 g, 10.18 mmol), anh. MeCN (9 ml), and tetramethylguanidinium azide (1.77 g, 11.19 mmol) was prepared at 0°. After stirring at 0° for 5 min, the soln. was poured into $CH_2Cl_2$ (1 l). The org. phase was washed rapidly with cooled 1N aq. HCl (100 ml, ice), dried ($MgSO_4$), and evaporated to give 3.7 g of an oil which was purified by FC (silica gel; AcOEt/PET 1 : 1): 3.37 g (93%) of (+)-**38** (storage at −22°). Slightly orange oil. $R_f$ (AcOEt/PET 2 : 1) 0.35. $[\alpha]^{25}_{589}=+192$, $[\alpha]^{25}_{577}=+210$, $[\alpha]^{25}_{546}=+231$, $[\alpha]^{25}_{435}=+417$, $[\alpha]^{25}_{405}=+516$ ($c=0.25$, $CHCl_3$). UV (MeCN): 199 (9400). IR (film): 3475, 2910, 2100, 1740, 1435, 1370, 1235, 1035, 905, 665. $^1$H-NMR (400 MHz, $CDCl_3$): 5.86 (br. *d*, $^3J=3.8$, H−C(4)); 4.69, 4.62 (2*d*, $^2J=13.7$, $CH_2$−C(3)); 4.46 (*dd*, $^2J=11.6$, $^3J=7.4$, 1 H); 4.41 (*dd*, $^2J=11.5$, $^3J=5.8$, 1 H); 4.15 (*dd*, $^2J=11.6$, $^3J=5.4$, 1 H, $CH_2$−C(1)); 4.23 (*dd*, $^2J=11.5$, $^3J=6.9$, 1 H, $CH_2$−C(2)); 3.94 (br. *dd*, $^3J=3.8$, 3.5, H−C(5)); 3.90 (br. *dd*, $^3J=3.5$, 2.6, H−C(6)); 2.75 (br. *ddd*, $^3J=6.9$, 6.0, 5.8, H−C(2)); 2.33 (*dddd*, $^3J=7.4$, 6.0, 5.4, 2.6, H−C(1)); 2.10, 2.09 (2*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 171.2, 170.4, 170.3 (3*m*, C=O); 138.5 (*s*, C(3)); 121.8 (*d*, $J=161$, C(4)); 69.0 (*d*, $J=148$, C(6)); 65.5 (*td*, $J=148$, 6.4, $CH_2$−C(3)); 63.5, 62.3 (2*t*, $J=150$, 141, 2 $CH_2$); 60.3 (*d*, $J=147$, C(5)); 37.8 (*d*, $J=130$, C(2)); 36.4 (*d*, $J=139$, C(1)); 20.9, 20.83, 20.81 (3*q*, $J=130$, 3 Me). CI-MS ($NH_3$): 91 (98), 120 (100), 147 (36), 163 (17), 178 (12), 193 (17), 253 (8), 313 (3), 356 (0.2 $M^+$). Anal. calc. for $C_{15}H_{23}N_3O_7$ (355.35): C 50.70, H 5.96; found: C 50.47, H 5.75.

*(1RS,2RS,5SR,6SR)-5-Azido-6-hydroxycyclohex-3-ene-1,2,3-trimethyl Triacetate* ((±)-**38**). As described for (+)-**38**, from (±)-**31**.

*(1R,2R,5S,6S)-5-Azido-6-hydroxycyclohex-3-ene-1,2,3-trimethanol* ((+)-**39**). Gaseous $NH_3$ was bubbled carefully through a soln. of (+)-**38** (100 mg, 0.283 mmol) in anh. MeOH (2 ml) for 15 min (pH control). After stirring at 20° for 14 h, the solvent was evaporated and the residue purified by FC (silica gel; AcOEt/PET 8 : 1): 55 mg (85%) of (+)-**39**. Colorless oil. $R_f$ (AcOEt/MeOH 8 : 1) 0.38. $[\alpha]^{25}_{589}=+263$, $[\alpha]^{25}_{577}=+284$, $[\alpha]^{25}_{546}=+339$, $[\alpha]^{25}_{435}=+613$, $[\alpha]^{25}_{405}=+754$ ($c=0.1$, $CHCl_3$). UV (MeCN): 209.6 (7500). IR (film): 3340, 2895, 2110, 1665, 1615, 1455, 1300, 1165, 1025, 900, 665. $^1$H-NMR (400 MHz, $CDCl_3$): 5.87 (br. *s*, H−C(4)); 4.20, 4.15 (2 br. *dm*, $^2J=14.0$, $^5J=1.6$, $CH_2$−C(3)); 3.84–3.82 (br. *m*, $CH_2$); 3.78 (*dd*, $^2J=11.7$, $^3J=7.4$, 1 H, $CH_2$−C(1)); 3.77 (*dd*, $^2J=11.9$, $^3J=4$, 1 H); 3.64 (*dd*, $^3J=2.2$, 1.6, H−C(6)); 3.31 (*dq*, $^3J={}^5J=1.6$, H−C(5)); 2.72 (br. *m*, $^3J=7.2$, H−C(2)); 2.20 (*dtd*, $^3J=7.4$, 7.2, 2.2, H−C(1)). $^{13}$C-NMR (100.6 MHz, $CD_3OD$): 145.6 (*s*, C(3)); 119.0 (*d*, $J=160$, C(4)); 68.9 (*d*, $J=150$, C(6)); 64.6 (*t*, $J=141$, $CH_2$−C(3)); 62.0 (*d*, $J=148$, C(5)); 61.6, 58.3 (2*t*, $J=141$, 142, 2 $CH_2$); 41.8 (*d*, $J=128$, C(2)); 38.9 (*d*, $J=124$, C(1)). CI-MS ($NH_3$): 80 (74), 91 (100),

108 (80), 122 (37), 151 (17), 169 (5), 208 (2), 230 (8). Anal. calc. for $C_9H_{15}N_3O_4$ (229.24): C 47.16, H 6.60; found: C 47.05, H 6.58.

*(1RS,2RS,5SR,6SR)-5-Azido-6-hydroxycyclohex-3-ene-1,2,3-trimethanol* ((±)-**39**). As described for (+)-**39**, from (±)-**38**.

*(1R,2R,5S,6S)-5-Amino-6-hydroxycyclohex-3-ene-1,2,3-trimethanol* ((+)-**40**). *Method A*: A mixture of (+)-**39** (16 mg, 0.07 mmol), anh. MeOH (0.5 ml), $Na_2S$ (36 mg, 0.147 mmol), and $Et_3N$ (1 µl) was stirred at 40° in the dark for 12 h (TLC control (silica gel; AcOEt/MeOH 8 : 1)). The suspension was then acidified with conc. HCl soln. and deposited on *Dowex-50WX8* ($H^+$ form). The resin was first washed with $H_2O$ (15 ml) and then with MeOH (15 ml). Elution with 5% aq. $NH_3$ soln. and evaporation of the basic fractions afforded 13.5 mg (95%) of (+)-**40**.

*Method B:* MeOH (5 ml) and 10% Pd/C (40 mg) were degassed and purged with $H_2$. The catalyst was activated for 30 min by shaking, then (+)-**39** (50 mg, 0.218 mmol) was added. After shaking for 15 min, the suspension was filtered through a *Celite* pad, and the catalyst was washed with MeOH (5 ml). Evaporation afforded 44 mg (97%) of (+)-**40**. Further purification by *Dowex* resin can be done as above. Slightly yellow oil. $[\alpha]^{25}_{589} = +77$, $[\alpha]^{25}_{577} = +535$, $[\alpha]^{25}_{546} = +124$, $[\alpha]^{25}_{435} = +210$, $[\alpha]^{25}_{405} = +243$ ($c = 0.08$, $CHCl_3$). IR (film): 3320, 3280, 2890, 1660, 1585, 1460, 1360, 1260, 1220, 1160, 1100, 1025, 985, 875, 665. $^1H$-NMR (400 MHz, $CD_3OD$): 5.81 (*s*, H–C(4)); 4.19, 4.09 (2*d*, $^2J = 13.1$, $CH_2$–C(3)); 3.85 (*d*, $^3J = 7.3$, $CH_2$–C(1)); 3.80 (*dd*, $^2J = 11.8$, $^3J = 4.5$, 1 H); 3.74 (br. *t*, $^3J = 2.5$, H–C(6)); 3.70 (*dd*, $^2J = 11.8$, $^3J = 2.7$, 1 H, $CH_2$–C(2)); 3.27 (br. *d*, $^3J = 2.5$, H–C(5)); 2.73 (br. *ddd*, $^3J = 7.0$, 4.5, 2.7, H–C(2)); 2.31 (br. *tdd*, $^3J = 7.3$, 7.0, 2.5, H–C(1)). $^{13}C$-NMR (100.6 MHz, $D_2O$): 139.9 (*s*, C(3)); 125.0 (*d*, $J = 162$, C(4)); 70.2 (*d*, $J = 145$, C(6)); 63.8 (*t*, $J = 143$, $CH_2$–C(3)); 60.7, 58.0 (2*t*, $J = 148$, 145, 2 $CH_2$); 51.8 (*d*, $J = 141$, C(5)); 39.7 (*d*, $J = 126$, C(2)); 37.8 (*d*, $J = 126$, C(1)). CI-MS ($NH_3$): 91 (100), 108 (84), 121 (28), 129 (24), 172 (10), 204 (51).

*(1RS,4SR,5SR,6RS)-Benzyl (6-Hydroxy-3,4,5-tris(hydroxymethyl)cyclohex-2-enyl)carbamate* ((±)-**41**). A mixture of (±)-**40** (10 mg, 0.049 mmol), 50% aq. EtOH (1 ml), $NaHCO_3$ (7.4 mg, 0.088 mmol), and benzylcarbonyl chloride (8 µl, 0.058 mmol) was stirred at 20° for 15 h. Evaporation and FC (silica gel; AcOEt/MeOH 8 : 1) gave 15 mg (90%) of (±)-**41**. Colorless oil. $R_f$ (AcOEt/MeOH 8 : 1) 0.20. UV (MeCN): 200.5 (11900). IR (film): 3320, 2895, 1695, 1540, 1505, 1455, 1305, 1250, 1130, 1030, 750, 665. $^1H$-NMR (400 MHz, $CD_3OD$): 7.31–7.25 (*m*, arom. H); 5.66 (*d*, $^3J = 4.7$, H–C(2)); 5.06, 5.02 (2*d*, $^2J = 12.3$, $PhCH_2$); 4.06, 4.03 (2*d*, $^2J = 13.5$, $CH_2$–C(3)); 4.01 (br. *s*, H–C(6)); 3.78–3.72 (*m*, $CH_2$, H–C(1)); 3.70 (*dd*, $^2J = 11.7$, $^3J = 4.3$, 1 H); 3.57 (*dd*, $^2J = 12.1$, $^3J = 1.9$, 1 H, $CH_2$); 2.62 (br. *m*, H–C(4)); 2.15 (br. *m*, H–C(5)). $^{13}C$-NMR (100.6 MHz, $CD_3OD$): 158.1 (*s*, C=O); 142.6 (*s*); 138.3 (*s*, C(3)); 129.5 (*dd*, $J = 160$, 5.5); 129.0, 128.9 (2*d*, $J = 157$, arom. C ar); 122.9 (*d*, $J = 159$, C(2)); 69.3 (*d*, $J = 147$, C(6)); 67.5, 64.9, 62.0, 58.3 (4*t*, $J = 141$, 141, 140, 145, 4 $CH_2$); 53.4 (*d*, $J = 141$, C(1)); 41.1 (*d*, $J = 126$, C(4)); 38.5 (*d*, $J = 125$, C(5)). CI-MS ($NH_3$): 91 (100), 108 (55), 152 (2), 241 (1), 301 (0.5), 320 (0.5), 338 (0.3). Anal. calc. for $C_{17}H_{23}NO_6$ (337.37): C 60.52, H 6.87; found: C 60.15, H 6.88.

*(1RS,2RS,5RS,6SR)-5-Bromo-3-(bromomethyl)-6-hydroxycyclohex-3-ene-1,2-dimethyl Diacetate* ((±)-**42**). $BBr_3$ (37 µl, 0.38 mmol) was added to a stirred soln. of (±)-**31** (0.1 g, 0.254 mmol) in anh. $CH_2Cl_2$ (1 ml) cooled to 0°. After 5 min at 0°, the soln. was stirred at 20° for 25 min. It was then diluted with $CH_2Cl_2$ (200 ml), washed with $H_2O$ (50 ml), dried ($MgSO_4$), and evaporated to afford 103 mg (98%) of (±)-**42**. An anal. sample was obtained by FC (silica gel; AcOEt/PET 1 : 1). Colorless, unstable oil that crystallized (storage in the freezer). $R_f$ (AcOEt/PET 2 : 1) 0.50. IR (film): 3470, 2960, 2925, 2905, 1735, 1655, 1485, 1465, 1400, 1360, 1340, 1265, 1230, 1180, 1155, 1100, 1040, 955, 945, 920, 880, 870, 850, 815, 755, 710, 650, 620, 605, 565, 520, 480. $^1H$-NMR (250 MHz, $CDCl_3$): 5.95 (br. *s*, H–C(4)); 4.86 (*dd*, $^3J = 4.5$, 1.6, H–C(5)); 4.60 (*dd*, $^2J = 11.8$, $^3J = 4.4$, 1 H); 4.45 (*dd*, $^2J = 11.5$, $^3J = 6.5$, 1 H); 4.38 (*dd*, $^2J = 11.5$, $^3J = 7.0$, 1 H, $CH_2$–C(1)); 4.31, 3.98 (2*d*, $^2J = 10.4$, $CH_2$–C(3)); 4.13 (*dd*, $^2J = 11.8$, $^3J = 6.8$, 1 H, $CH_2$–C(2)); 4.06 (br. *d*, $^3J = 4.5$, H–C(6)); 2.92 (br. *ddd*, $^3J = 6.8$, 6.0, 4.4, $^5J = 1.6$, H–C(2)); 2.45 (br. *s*, OH); 2.33 (br. *ddd*, $^3J = 7.0$, 6.5, 6.0, H–C(1)); 2.10, 2.09 (2*s*, 2 Me). $^{13}C$-NMR (100.6 MHz, $CDCl_3$): 183.0 (*m*, C=O); 139.4 (*s*, C(3)); 127.3 (*d*, $J = 159$, C(4)); 66.2 (*d*, $J = 151$, C(6)); 64.5, 63.4 (2*t*, $J = 150$, 153, $CH_2$); 54.6 (*d*, $J = 153$, C(5)); 40.9 (*d*, $J = 124$, C(2)); 35.7 (*t*, $J = 148$, $CH_2$–C(3)); 35.0 (*d*, $J = 125$, C(1)); 21.09, 20.9 (2*q*, $J = 129$, 2 Me). CI-MS ($NH_3$): 91 (11), 105 (13), 117 (33), 121 (15), 134 (22), 177 (92), 237 (100), 253 (18), 255 (20), 272 (33), 353 (27), 355 (53), 357 (27), 430 (41), 432 (81), 434 (38).

*(1RS,2RS,5SR,6SR)-5-Azido-3-(azidomethyl)-6-hydroxycyclohex-3-ene-1,2-dimethyl Diacetate* ((±)-**43**). Tetramethylguanidinium azide (80.3 mg, 0.507 mmol) was added in one portion to a soln. of (±)-**42** (100 mg, 0.242 mmol) in dry MeCN/DMF 4 : 1 (1.5 ml) at 0° under Ar. The soln. was stirred at 0° for 10 min and at 20° for 10 min. It was diluted with AcOEt (100 ml), washed with aq. 1N HCl (30 ml) and aq. sat. NaCl soln. (10 ml), dried ($MgSO_4$), and evaporated. If necessary, the crude residue could be purified by FC (silica gel; AcOEt/PET 1 : 1): 57 mg (80%) of (±)-**43** (storage at −22°). Colorless oil. $R_f$ (AcOEt/PET 2 : 1) 0.40. IR (film): 3475, 2965,

2910, 2105, 1740, 1435, 1370, 1245, 1155, 1105, 1040, 980, 920, 850. $^1$H-NMR (400 MHz, $CDCl_3$): 5.84 (br. *s*, H−C(4)); 4.48 (*dd*, $^2J = 11.4$, $^3J = 7.4$, 1 H); 4.45 (*dd*, $^2J = 11.9$, $^3J = 5.4$, 1 H); 4.23 (*dd*, $^2J = 11.4$, $^3J = 7.0$, 1 H, $CH_2$−C(1)); 4.14 (*dd*, $^2J = 11.9$, $^3J = 5.1$, 1 H, $CH_2$−C(2)); 3.95 (*s*, $CH_2$−$N_3$, H−C(6)); 3.90 (br. *s*, H−C(5)); 2.74 (br. *ddd*, $^3J = 5.4$, 5.1, 5.8, H−C(2)); 2.33 (*dddd*, $^3J = 7.4$, 7.0, 5.8, 2.6, H−C(1)); 2.10, 2.08 (2*s*, 2 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 171.3, 170.3 (2*s*, C=O); 138.2 (*s*, C(3)); 122.3 (*d*, $J = 161$, C(4)); 68.9 (*d*, $J = 149$, C(6)); 63.4, 62.3 (2*t*, $J = 151$, 148, 2 $CH_2$); 60.4 (*d*, $J = 146$, C(5)); 54.9 (*dt*, $J = 6.4$, 145, $CH_2$−$N_3$); 37.8 (*d*, $J = 125$, C(2)); 36.5 (*d*, $J = 125$, C(1)); 20.9, 20.8 (2*q*, $J = 134$, 2 Me). CI-MS ($NH_3$): 80 (75), 91 (100), 106 (95), 148 (26), 189 (13), 236 (4), 296 (11), 315 (7), 356 (5). Anal. calc. for $C_{13}H_{18}N_6O_5$ (338.32): C 46.15, H 5.36; found: C 45.75, H 5.29.

*(1RS,2RS,5SR,6SR)-5-Azido-3-(azidomethyl)-6-hydroxycyclohex-3-ene-1,2-dimethanol* ((±)-**44**). Gaseous $NH_3$ was bubbled carefully through a soln. of (±)-**43** (83 mg, 0.28 mmol) in anh. MeOH (2 ml) for *ca.* 10 s (pH control). After stirring at 20° for 12 h (TLC control (silica gel; AcOEt/MeOH 8 : 1)), the solvent was evaporated and the crude product purified by FC (silica gel; AcOEt/MeOH 8 : 1): 61 mg (96%) of (±)-**44**. Colorless oil. $R_f$ (AcOEt) 0.32. UV (MeCN): 192.3 (1000). IR (film): 3290, 2920, 2895, 2105, 1735, 1600, 1450, 1245, 1165, 1075, 1030, 915. $^1$H-NMR (400 MHz, $CDCl_3$): 5.91 (br. *d*, $^3J = 3.0$, H−C(4)); 4.00 – 3.95 (*m*, 1 H of $CH_2$−C(1), H−C(5), H−C(6)); 4.00 (*dd*, $^2J = 11.0$, $^3J = 6.0$, 1 H of $CH_2$−C(1)); 3.91 (*dd*, $^2J = 11.9$, $^3J = 4.4$, 1 H); 3.86 (*dd*, $^2J = 11.9$, $^3J = 2.2$, 1 H, $CH_2$−C(2)); 2.68 (br. *ddd*, $^3J = 6.4$, 4.4, 2.2, H−C(2)); 2.41 (br. *s*, OH); 2.27 (*dddd*, $^3J = 6.4$, 6.0, 6.0, 2.5, H−C(1)). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 138.1 (*s*, C(3)); 123.7 (*d*, $J = 160$, C(4)); 68.5 (*d*, $J = 151$, C(6)); 61.9, 58.2 (2*t*, $J = 143$, 144, 2 $CH_2$); 60.4 (*d*, $J = 150$, C(5)); 54.9 (*dt*, $J = 6.4$, 144, $CH_2$−C(3)); 39.9 (*d*, $J = 125$, C(2)); 39.0 (*d*, $J = 122$, C(1)). CI-MS ($NH_3$): 80 (77), 91 (100), 94 (83), 106 (93), 122 (39), 154 (5). Anal. calc. for $C_9H_{14}N_6O_3$ (254.25): C 45.52, H 5.55; found: C 45.47, H 5.61.

*(1RS,2RS,5SR,6SR)-5-Amino-3-(aminomethyl)-6-hydroxycyclohex-3-ene-1,2-dimethanol* ((±)-**45**). For 30 min, 10% Pd/C (10 mg) in MeOH (4 ml) was activated by shaking under $H_2$. Then (±)-**44** (38 mg, 0.15 mmol) was added. The suspension was shaken until no starting material remained (TLC control (silica gel; AcOEt/MeOH 8 : 1)), then it was filtered through a *Celite* pad and evaporated. The crude product was dissolved in 1N HCl in $H_2O$/MeOH 1 : 1 (200 µl) and loaded onto *Dowex 50WX-8* resin ($H^+$ form). The resin was washed with $H_2O$ (20 ml) and then with MeOH (20 ml). Elution with 5% $NH_3$ soln. and evaporation of the alkaline fractions afforded 25.7 mg (85%) of (±)-**45**. Colorless oil. $R_f$ (MeOH/$NH_3$ 5% 10 : 1) 0.067. IR (film): 3345, 2890, 1645, 1560, 1570, 1470, 1455, 1410, 1095, 1025. $^1$H-NMR (400 MHz, $CD_3OD$): 5.66 (br. *d*, $^3J = 3.0$, H−C(4)); 3.77 (*d*, $^3J = 7.3$, $CH_2$−C(1)); 3.71 (*dd*, $^2J = 12.0$, $^3J = 4.0$, 1 H); 3.65 (br. *dd*, $^3J = 3.0$, 2.5, H−C(6)); 3.61 (*dd*, $^2J = 12.0$, $^3J = 2.9$, 1 H, $CH_2$−C(2)); 3.28, 3.24 (2*d*, $^2J = 16.0$, $CH_2$−C(3)); 3.19 (br. *t*, $^3J = 3.0$, H−C(5)); 2.55 (br. *ddd*, $^3J = 4.0$, 2.9, 2.5, H−C(2)); 2.22 (*tdd*, $^3J = 7.3$, 7.0, 2.5, H−C(1)). $^{13}$C-NMR (100.6 MHz, $CD_3OD$): 141.0 (*s*, C(3)); 126.3 (*d*, $J = 156$, C(4)); 72.6 (*d*, $J = 147$, C(6)); 61.7, 59.1 (2*t*, $J = 139$, 143, 2 $CH_2$); 53.6 (*d*, $J = 137$, C(5)); 46.0 (*t*, $J = 129$, $CH_2$−C(3)); 41.7 (*d*, $J = 125$, C(5)); 40.7 (*d*, $J = 122$, C(6)). CI-MS ($NH_3$): 81 (62), 91 (71), 106 (100), 149 (9), 168 (11), 186 (11), 203 (5).

*(1RS,4SR,5SR,6RS)-Benzyl (6-Hydroxy-4,5-bis(hydroxymethyl)-3-{{[(phenylmethoxy)carbonyl]amino}methyl}cyclohex-2-enyl)carbamate* ((±)-**46**). To a soln. of (±)-**45** (8 mg, 0.040 mmol) in 50% aq. EtOH soln. (0.5 ml), $NaHCO_3$ (10 mg, 0.119 mmol) and benzyl carbonochloridate (CbzCl; 13.5 µl, 0.095 mmol) were added. The mixture was stirred at 20° for 1 h. After evaporation, the residue was purified by FC (silica gel; AcOEt/MeOH 8 : 1): 15.5 mg (83%) of (±)-**46**. White solid (needles, MeOH/$CH_2Cl_2$/PET). M.p. 61 – 62°. $R_f$ (AcOEt/MeOH 8 : 1) 0.50. UV (MeCN): 205.4 (20100). IR (KBr): 3340, 3035, 2895, 1700, 1675, 1525, 1455, 1435, 1295, 1255, 1165, 1020, 910, 750, 730, 695. $^1$H-NMR (400 MHz, $CD_3OD$): 7.37 – 7.24 (*m*, 10 arom. H); 5.59 (*d*, $^3J = 4.3$, H−C(2)); 5.09, 5.04 (2*d*, $^2J = 12.4$, 2 Bn); 4.01 (br. *s*, H−C(6)); 3.86, 3.69 (2*d*, $^2J = 16.2$, $CH_2$−C(3)); 3.78 – 3.65 (*m*, 2 $CH_2$, H−C(1)); 2.49 (br. *m*, H−C(4)); 2.17 (br. *t*, $^3J = 7.0$, H−C(5)). $^{13}$C-NMR (100.6 MHz, $CD_3OD$): 159.1, 157.9 (2*s*, C=O); 140.3, 138.3 (2*s*, arom. C); 129.5, 129.0, 128.9 (3*d*, $J = 160$, 3 arom. C); 128.7 (*s*, C(3)); 123.0 (*d*, $J = 153$, C(2)); 68.9 (*d*, $J = 149$, C(6)); 67.6, 67.5 (2*t*, $J = 145$, 2 $PhCH_2$); 62.1, 57.9 (2*t*, $J = 142$, 144, 2 $CH_2$); 53.4 (*d*, $J = 141$, C(1)); 45.4 (*t*, $J = 137$, $CH_2$−C(3)); 40.8 (*d*, $J = 127$, C(4)); 39.0 (*d*, $J = 126$, C(5)). CI-MS ($NH_3$): 79 (79), 91 (60), 108 (100), 242 (0.4), 301 (0.1), 471 (0.1). Anal. calc. for $C_{25}H_{30}N_2O_7$ (470.52): C 63.82, H 6.43; found: C 63.72, H 6.34.

*(1RS,2RS,3SR,4RS,5SR,6RS)-5-Azido-1,4,6-trihydroxycyclohexane-1,2,3-trimethyl Triacetate* ((±)-**47**). To a vigorously stirred soln. of (±)-**38** (100 mg, 0.283 mmol) in AcOEt/MeCN 1 : 1 (5 ml) at 0 – 5° (ice-water bath), a soln. of $RuCl_3$ hydrate (41% Ru, 0.012 mmol) and $NaIO_4$ (90.8 mg, 0.425 mmol) in distilled $H_2O$ (700 µl) was added dropwise. The two-phase mixture was stirred vigorously for 1 min and quenched with a cooled sat. aq. $Na_2S_2O_3$ soln. (10 ml). The aq. phase was immediately extracted with AcOEt (50 ml, 3 times). The combined org. phases were dried ($MgSO_4$) and evaporated and the dark residue containing two isomers (6.3 : 1) submitted to FC (silica gel; 10°, AcOEt/PET 2 : 1): 41 mg (47%) of pure major isomer (±)-**47** and 49 mg (44%)

of a mixture. Colorless oil. Data of (±)-**47**: $R_f$ (AcOEt/PET) 0.15. IR (film) 3440, 2970, 2920, 2110, 1730, 1470, 1435, 1370, 1250, 1130, 1040, 665. $^1$H-NMR (400 MHz, $CDCl_3$): 4.50 (*dd*, $^2J = 12.2$, $^3J = 5.7$, 1 H); 4.45 (*dd*, $^2J = 12.2$, $^3J = 4.8$, 1 H, $CH_2-C(3)$); 4.37 (*d*, $^3J = 6.8$, $CH_2$); 4.27, 3.90 (2*d*, $^2J = 11.5$, $CH_2-C(1)$); 3.64 (*dd*, $^3J = 10.5$, 9.0, H−C(5)); 3.59 (*dd*, $^3J = 10.5$, 4.9, H−C(4)); 3.50 (br. *s*, OH); 3.31 (*d*, $^3J = 9.0$, H−C(6)); 3.00 (br. *s*, OH); 2.58 (*dddd*, $^3J = 5.7$, 5.0, 4.9, 4.8, H−C(3)); 2.09, 2.06, 2.04 (3*s*, Me); 2.09–2.00 (*m*, $^3J = 5.0$, H−C(2)). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 171.3, 171.2, 170.9 (3*s*, C=O); 73.9 (*s*, C(1)); 72.4, 72.2 (2*d*, $J = 141$, 146, C(6), C(4)); 65.4 (*d*, $J = 140$, C(5)); 62.8 (*dd*, $J = 149$, 152, $CH_2-C(1)$); 61.7, 61.5 (2*t*, $J = 149$, 2 $CH_2$); 40.7, 37.9 (2*d*, $J = 132$, 129, C(2), C(3)); 21.1, 20.8 (2*q*, $J = 130$, 2 Me). CI-MS ($NH_3$): 70(100), 108(52), 136(60), 183(24), 209(12), 256(13), 312(37), 330(44), 37(8), 372(36), 390(13), 407(22). Anal. calc. for $C_{15}H_{23}N_3O_9$ (389.40): C 6.27, H 5.95, N 10.79; found: C 46.19, H 5.99, N 10.67.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*)-5-Azido-1,4,6-trihydroxycyclohexane-1,2,3-trimethanol* ((±)-**48**). Gaseous $NH_3$ was bubbled through a soln. of (±)-**47** (50 mg, 0.128 mmol) in anh. MeOH (2 ml) and the soln. stirred at 20° for 16 h. MeOH was then evaporated to afford a mixture of (±)-**48** (100%) and acetamide. FC (silica gel; AcOEt/MeOH 8 : 1) gave 30.6 mg (91%) of pure (±)-**48**. Slightly yellow oil that partially crystallized in the freezer. $R_f$ (AcOEt/MeOH 8 : 1) 0.30. IR (film): 3550, 2900, 2110, 1700, 1665, 1375, 1255, 1040, 885. $^1$H-NMR (400 MHz, $D_2O$): 3.85 (*dd*, $^2J = 11.5$, $^3J = 5.3$, 1 H); 3.84 (*dd*, $^2J = 11.5$, $^3J = 3.4$, 1 H); 3.70 (*dd*, $^2J = 11.5$, $^3J = 3.8$, 1 H, $CH_2-C(3)$); 3.72 (*dd*, $^3J = 10.5$, 10.0, H−C(5)); 3.66 (*dd*, $^2J = 11.5$, $^3J = 8.5$, 1 H, $CH_2-C(2)$); 3.56 (*dd*, $^3J = 10.5$, 6.0, H−C(4)); 3.34 (*d*, $^3J = 10.0$, H−C(6)); 3.58, 3.36 (2*d*, $^2J = 11.5$, $CH_2-C(1)$); 2.30 (br. *dddd*, $^3J = 6.0$, 5.3, 3.8, 3.4, H−C(3)); 1.96 (*ddd*, $^3J = 8.5$, 5.3, 5.3, H−C(2)). $^{13}$C-NMR (100.6 MHz, $CD_3OD$): 75.5 (*s*, C(1)); 74.0, 73.9 (2*d*, $J = 143$, C(4), C(6)); 69.1 (*d*, $J = 144$, C(5)); 62.6 (*t*, $J = 143$, $CH_2-C(1)$); 60.1, 58.2 (2*t*, $J = 134$, 141, 2 $CH_2$); 43.7, 41.6 (2*d*, $J = 127$, 122, C(2), C(3)). Anal. calc. for $C_9H_{17}N_3O_6$ (263.30) containing 2% of $H_2O$ (as titrated by the *Karl Fischer* technique): C 41.06, H 6.51; found: C 39.99, H 6.46.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*)-5-Amino-1,4,6-trihydroxycyclohexane-1,2,3-trimethanol* ((±)-**49**). A mixture of (±)-**48** (11.7 mg, 0.044 mmol), MeOH (0.5 ml), and 20% Pd/C (4 mg) was degassed and shaken under $H_2$ at 20° for 15 h. The soln. was filtered through a *Celite* pad and evaporated. The residue was dissolved in 1N HCl in $H_2O$/MeOH 1 : 1 (100 μl) and deposited on *Dowex 50 WX-8* ($H^+$ form). The resin was washed with $H_2O$ (10 ml) and then with MeOH (10 ml). Elution with 5% aq. $NH_3$ soln. and evaporation of the alkaline fraction gave 0.5 mg (90%) of pure (±)-**49**. Colorless oil. IR (film): 3350, 2900, 1650, 1585, 1465, 1415, 1235, 1085, 1045, 882. $^1$H-NMR (400 MHz, $D_2O$): 4.01 (*dd*, $^2J = 11.5$, $^3J = 5.6$, 1 H); 3.98 (*dd*, $^2J = 12.2$, $^3J = 3.0$, 1 H); 3.87 (*dd*, $^2J = 12.2$, $^3J = 5.0$, 1 H, $CH_2-C(3)$); 3.82 (*dd*, $^2J = 11.5$, $^3J = 8.5$, 1 H, $CH_2-C(2)$); 3.71, 3.51 (2*d*, $^2J = 11.4$, $CH_2-C(1)$); 3.62 (*dd*, $^3J = 10.5$, 5.9, H−C(4)); 3.34 (*d*, $^3J = 10.5$, H−C(6)); 3.19 (*t*, $^3J = 10.5$, H−C(5)); 2.41 (*dddd*, $^3J = 5.9$, 5.6, 5.0, 3.0, H−C(3)); 2.11 (*ddd*, $^3J = 8.5$, 5.6, 5.6, H−C(2)). $^{13}$C-NMR (100.6 MHz, $D_2O$): 76.5 (*s*, C(1)); 74.1, 74.0 (2*d*, $J = 141$, C(4), C(6)); 63.0 (*t*, $J = 145$, $CH_2-C(1)$); 60.8, 59.1 (2*t*, $J = 143$, 145, 2 $CH_2$); 56.4 (*d*, $J = 148$, C(5)); 43.9, 42.3 (2*d*, $J = 131$, 125, C(2), C(3)). CI-MS ($NH_3$): 81(40), 91(56), 108(38), 122(34), 136(15), 170(12), 188(93), 202(16), 220(33), 238(100).

*(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*)-5-Acetamido-4,6-diacetoxy-1-hydroxycyclohexane-1,2,3-trimethyl Triacetate* ((±)-**50**. A mixture of (±)-**49** (10 mg, 0.042 mmol) in dry pyridine/$Ac_2O$ 1 : 1 (0.1 ml) was stirred at 20° for 24 h. The solvents were evaporated with toluene (2 ml, 3 times). The residue was purified by FC (silica gel; AcOEt): 16 mg (77%) of (±)-**52**. Colorless oil. IR (film): 3355, 2925, 1740, 1665, 1550, 1435, 1370, 1240, 1195, 1095, 1035, 980, 730. $^1$H-NMR (400 MHz, $CDCl_3$): 5.41 (*d*, $^3J = 9.8$, NH); 4.89 (*dd*, $^3J = 11.0$, 5.5, H−C(4)); 4.88 (*d*, $^3J = 10.6$, H−C(6)); 4.63 (*ddd*, $^3J = 11.0$, 10.6, 9.8, H−C(5)); 4.54 (*dd*, $^2J = 12.3$, $^3J = 4.2$, 1 H); 4.41 (*dd*, $^2J = 12.3$, $^3J = 6.1$, 1 H, $CH_2-C(3)$); 4.39 (*d*, $^3J = 6.7$, $CH_2-C(2)$); 3.97, 3.93 (2*d*, $^2J = 11.6$, $CH_2-C(1)$); 2.79 (*s*, OH); 2.68 (*dddd*, $^3J = 6.1$, 6.0, 5.5, 4.2, H−C(3)); 2.27 (*td*, $^3J = 6.7$, 6.0, H−C(2)); 2.09–2.02 (5*s*, 6 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 171.0, 170.6, 170.4, 170.0 (5*s*, C=O); 73.7 (*s*, C(1)); 72.9, 72.0 (2*d*, $J = 154$, 145, C(2), C(4)); 62.3, 61.4, 61.2 (3*t*, $J = 148$, 146, 145, $CH_2$); 48.8 (*d*, $J = 137$, C(3)); 38.9, 38.5 (2*d*, $J = 129$, 127, C(5), C(6)); 23.2 (*q*, $J = 129$, 6 Me). CI-MS ($NH_3$): 72(47), 135(28), 236(9), 296(25), 356(309, 430(30), 490(100). Anal. calc. for $C_{21}H_{31}NO_{12}$ (489.48): C 51.53, H 6.38; found: C 51.75, H 6.21.

*(1*RS*,2*RS*,5*RS*)-5-Bromo-6-oxocyclohex-3-ene-1,2,3-trimethyl Triacetate* ((±)-**51**). A mixture of (±)-**31** (21 mg, 0.053 mmol), $CH_2Cl_2$ (2 ml), and 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (45 mg, 0.107 mmol) was stirred overnight at 20°, diluted with $CH_2Cl_2$ (100 ml), washed successively with 5% aq. $Na_2S_2O_3$ soln. (20 ml), sat. aq. $NaHCO_3$ soln. (20 ml), and $H_2O$ (20 ml). Drying ($MgSO_4$) and evaporation gave 20 mg (96%) of (±)-**51**. Colorless, unstable oil (storage at −28°). IR (film): 2920, 1740, 1435, 1370, 1230, 1040, 975, 870, 725. $^1$H-NMR (250 MHz, $CDCl_3$): 6.16 (br. *d*, $^3J = 3.9$, H−C(4)); 5.18 (br. *d*, $^3J = 3.9$, H−C(5)); 4.74 (*d*, $^2J = 13.8$, 1 H); 4.64 (br. *d*, $^2J = 13.8$, $CH_2-C(3)$); 4.64 (*dd*, $^2J = 11.5$, $^3J = 5.8$, 1 H); 4.19 (*dd*, $^2J = 11.0$, $^3J = 3.0$, 1 H); 4.18 (*dd*, $^2J = 11.0$, $^3J = 3.1$, 1 H, $CH_2-C(2)$); 4.17 (*dd*, $^2J = 11.5$, $^3J = 8.2$, 1 H, $CH_2-C(1)$); 3.25 (*ddd*, $^3J = 8.2$, 6.0, 5.8, H−C(1)); 3.00 (*ddd*, $^3J = 6.0$, 3.1, 3.0, H−C(2)); 2.13, 2.07, 2.04 (3*s*, 3 Me). $^{13}$C-NMR

(100.6 MHz, $CDCl_3$): 198.5 (*s*, C(6)); 170.5 (*m*, C=O); 136.6 (*s*, C(3)); 128.4 (*dq*, *J* = 167, 6.4, C(4)); 60.4, 60.3, 64.7 (3*t*, *J* = 153, 153, 148, 3 $CH_2$); 48.8 (*d*, *J* = 126, C(5)); 47.8 (*d*, *J* = 148, C(1)); 39.5 (*d*, *J* = 134, C(2)); 20.82, 20.76 (2*q*, *J* = 139, 2 Me). CI-MS ($NH_3$): 77 (17), 91 (39), 120 (100), 149 (32), 210 (13), 273 (4), 311 (5).

*(1*RS*,2*SR*,3*SR*,6*SR*)-7-Oxabicyclo[4.1.0]hept-4-ene-2,3,4-trimethyl Triacetate* ((±)-**52**). A mixture of (±)-**31** (100 mg, 0.25 mmol), toluene (2.5 ml), and DBU (37 µl, 0.25 mmol) was stirred at 20° for 40 min, then the resulting suspension was filtered. Evaporation under high vacuum gave 78 mg (100%) of (±)-**52**. Colorless oil. $R_f$ (AcOEt/PET 2 : 1) 0.30. IR (film): 2925, 2955, 1740, 1665, 1650, 1435, 1370, 1230, 1035, 870. $^1$H-NMR (250 MHz, $CDCl_3$): 6.10 (*dt*, $^3J$ = 4.2, $^4J$ = 1.4, H–C(5)); 4.67, 4.60 (2*dd*, $^2J$ = 12.4, $^4J$ = 1.4, $CH_2$–C(4)); 4.50 (*dd*, $^2J$ = 11.2, $^3J$ = 7.2, 1 H); 4.40 (*dd*, $^2J$ = 11.2, $^3J$ = 7.8, 1 H, $CH_2$–C(2)); 4.27 (*dd*, $^2J$ = 11.3, $^3J$ = 6.6, 1 H); 4.09 (*dd*, $^2J$ = 11.3, $^3J$ = 5.6, 1 H, $CH_2$–C(3)); 3.52 (*dd*, $^3J$ = 4.2, 2.0, H–C(1)); 3.39 (*t*, $^3J$ = 4.2, H–C(6)); 2.62 (*dddd*, $^3J$ = 7.0, 6.6, 5.6, 2.0, H–C(3)); 2.27 (*ddd*, $^3J$ = 7.8, 7.2, 7.0, H–C(2)); 2.12, 2.11, 2.05 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.7, 170.4 (2*s*, C=O); 140.5 (*s*, C(4)); 122.3 (*d*, *J* = 162, C(5)); 66.9, 65.8, 63.7 (3*t*, *J* = 151, 148, 148, 3 $CH_2$): 55.9 (*d*, *J* = 175, C(6)); 47.0 (*dd*, *J* = 180, 7.6, C(1)); 37.2 (*d*, *J* = 134, C(3)); 35.9 (*d*, *J* = 125, C(2)); 20.9, 20.83, 20.8 (3*q*, *J* = 129, 3 Me). CI-MS ($NH_3$): 91 (44), 104 (100), 120 (79), 150 (30), 163 (12), 179 (3), 193 (8), 210 (5), 235 (1). Anal. calc. for $C_{15}H_{20}O_7$ (312.32): C 57.69, H 6.45; found: C 57.50, H 6.41.

*(1*RS*,2*SR*,3*RS*,4*SR*,5*SR*,6*SR*)-5-Bromo-1,4,6-trihydroxycyclohexane-1,2,3-trimethyl Triacetate* ((±)-**53**). A soln. of $RuCl_3 \cdot H_2O$ (41% Ru, 0.0178 mmol) and $NaIO_4$ (81 mg, 0.38 mmol) in $H_2O$ (0.7 ml) was added to a vigorously stirred soln. of (±)-**31** (100 mg, 0.254 mmol) in AcOEt/MeCN 1 : 1 (5 ml) at 0–5° (ice-water bath). The two-phase mixture was stirred vigorously for 1 min and quenched with a cooled sat. aq. $Na_2S_2O_3$ soln. (10 ml). The aq. phase was immediately extracted with AcOEt (50 ml, 3 times). The combined org. phases were dried ($MgSO_4$) and evaporated and the dark residue submitted to FC (silica gel; AcOEt/PET 2 : 1): 97.8 mg (90%) of (±)-**53**. Colorless crystals. M.p. 127–128°. $R_f$ (AcOEt/PET 2 : 1) 0.15. UV (MeCN): 206 (3090), 201 (3295), 199 (3390). IR (KBr): 3510, 2975, 1740, 1370, 1370, 1230, 1125, 1080, 1040, 985, 955, 940, 855, 710, 650, 610, 465. $^1$H-NMR (250 MHz, $CDCl_3$): 4.47, 4.14 (2*d*, $^2J$ = 12.0, $CH_2$–C(1)); 4.44 (*dd*, $^2J$ = 11.3, $^3J$ = 2.4, 1 H); 4.39 (*dd*, $^3J$ = 10.2, 2.9, H–C(5)); 4.30 (*dd*, $^2J$ = 12.9, $^3J$ = 3.3, 1 H); 4.24 (*dd*, $^2J$ = 11.3, $^3J$ = 5.5, 1 H, $CH_2$–C(3)); 4.13 (*dd*, $^2J$ = 12.9, $^3J$ = 8.0, 1 H, $CH_2$–C(2)); 4.11 (br. *dd*, $^3J$ = 4.5, 2.9, H–C(4)); 4.02 (*dd*, $^3J$ = 10.2, 4.5, H–C(6)); 2.75 (*d*, $^3J$ = 4.5, OH–C(4)); 2.89 (*s*, OH–C(1)); 2.96 (*d*, $^3J$ = 4.5, OH–C(6)); 2.67 (br. *ddd*, $^3J$ = 5.5, 4.5, 2.4, H–C(3)); 2.39 (*ddd*, $^3J$ = 8.0, 4.5, 3.3, H–C(2)); 2.10, 2.08, 2.01 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 171.3, 171.0, 170.7 (3*s*, C=O); 75.4 (*s*, C(1)); 70.5, 70.0 (2*d*, *J* = 149, 153, C(4), C(6)); 67.1 (*t*, *J* = 148, $CH_2$–C(1)); 63.3, 62.0 (2*td*, *J* = 151, 8, 2 $CH_2$); 62.9 (*d*, *J* = 153, C(5)); 42.7, 38.0 (2*d*, *J* = 127, 133, C(2), C(3)); 20.9 (*q*, *J* = 130, 3 Me). CI-MS ($NH_3$): 110 (2), 167 (4), 209 (5), 289 (11), 351 (44), 369 (96), 411 (6), 427 (6). Anal. calc. for $C_{15}H_{23}BrO_9$ (427.20): C 42.17, H 5.43, Br 18.70; found: C 42.03, H 5.40, Br 18.66.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*)-2,5-Dihydroxy-7-oxabicyclo[4.1.0]heptane-2,3,4-trimethyl Triacetate* ((±)-**54**). A mixture of (±)-**53** (214 mg, 0.5 mmol), MeCN (4 ml), BEMP (2-[(*tert*-butyl)imino]-2-(diethylamino)-1,3-dimethylperhydro-1,3,2-diazaphosphorine) on resin (2.3 mmol/g) was stirred at 40° for 2 d. The suspension was filtered, washed with MeCN (4 ml), and evaporated. The residue was purified by FC (*Florisil*; AcOEt/PET 2 : 1, 10°): 75 mg (44%) of (±)-**54**. Colorless oil. $R_f$ (AcOEt/PET 2 : 1) 0.10. IR ($CH_2Cl_2$): 3460, 2920, 2850, 2285, 1730, 1435, 1370, 1240, 1170, 1040, 940. $^1$H-NMR (250 MHz, $CDCl_3$): 4.71 (*dd*, $^2J$ = 11.3, $^3J$ = 9.6, 1 H); 4.30 (*dd*, $^2J$ = 12.0, $^3J$ = 3.4, 1 H); 4.26 (*d*, $^3J$ = 4.1, $CH_2$–C(2)); 4.16 (br. *ddd*, $^3J$ = 4.9, 2.8, 1.5, H–C(5)); 3.99 (*dd*, $^2J$ = 11.3, $^3J$ = 5.4, $CH_2$–C(4)); 3.94 (*dd*, $^2J$ = 12.0, $^3J$ = 8.5, $CH_2$–C(3)); 3.49 (*dd*, $^3J$ = 3.4, 1.5, H–C(6)); 3.33 (*d*, $^3J$ = 4.9, OH–C(5)); 3.23 (*d*, $^3J$ = 3.4, H–C(1)); 2.94 (*s*, OH–C(2)); 2.14, 2.10, 2.00 (3*s*, 3 Me); 2.12 (*dddd*, $^3J$ = 9.5, 5.4, 3.0, 2.8, H–C(4)); 1.91 (*ddd*, $^3J$ = 8.5, 3.4, 3.0, H–C(3)). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 172.3, 170.8 (2*s*, C=O); 69.2 (*s*, C(2)); 63.6 (*d*, *J* = 144, C(5)); 63.2, 61.3 (2*t*, *J* = 150, $CH_2$); 57.3, 54.1 (2*d*, *J* = 180, 170, C(1), C(6)); 42.0, 33.1 (2*d*, *J* = 133, 129, C(3), C(4)); 21.0, 20.9 (*q*, *J* = 129, 3 Me). CI-MS ($NH_3$): 148 (1), 190 (2), 227 (2), 269 (3), 304 (2), 348 (6), 364 (100). Anal. calc. for $C_{15}H_{22}O_9$ (346.34): C 52.02, H 6.40; found: C 52.17, H 6.54.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*)-2,5-Dihydroxy-7-oxabicyclo[4.1.0]heptane-2,3,4-trimethanol* ((±)-**55**). $NH_3$ was carefully bubbled through a soln. of (±)-**54** (23.4 mg, 0.068 mmol) in dry MeOH (1.5 ml) at 0° for *ca.* 10 s. The soln. was stirred at 20° for 20 h. The solvent was quickly evaporated (30°) to afford (±)-**55** contaminated with acetamide. FC (*Florisil*; AcOEt/MeOH 8 : 1) gave 10 mg (70%) of (±)-**55**. Colorless, unstable oil. $R_f$ (AcOEt/MeOH 8 : 1) 0.18. IR (film): 3355, 2920, 1725, 1650, 1465, 1430, 1370, 1265, 1165, 1065, 1020, 920, 855, 665. $^1$H-NMR (400 MHz, $CD_3OD$): 4.15 (*dd*, $^3J$ = 3.6, 1.7, H–C(5)); 3.81, 3.74 (2*d*, $^2J$ = 11.4, $CH_2$–C(2)); 3.80 (*dd*, $^2J$ = 10.9, $^3J$ = 6.6, 1 H); 3.69 (*dd*, $^2J$ = 12.5, $^3J$ = 3.4, 1 H); 3.62 (*dd*, $^2J$ = 10.9, $^3J$ = 7.5, $CH_2$–C(4)); 3.54 (*dd*, $^2J$ = 12.5, $^3J$ = 3.7, 1 H, $CH_2$–C(3)); 3.22 (*dd*, $^3J$ = 3.6, 1.7, H–C(6)); 3.09 (*d*, $^3J$ = 3.6, H–C(1)); 2.15

(*dddd*, $^3J = 7.5$, 6.6, 3.6, 3.6, H–C(4)); 1.69 (*ddd*, $^3J = 3.7$, 3.6, 3.4, H–C(3)). $^{13}$C-NMR (100.6 MHz, $CD_3OD$): 71.8 (*s*, C(2)); 68.0 (*t*, $J = 143$, $CH_2$–C(2)); 65.3 (*d*, $J = 145$, C(5)); 61.9, 58.1 (2*t*, $J = 141$, 137, 2 $CH_2$); 57.9, 56.7 (2*d*, $J = 177$, 178, C(1), C(6)); 43.9, 36.7 (2*d*, $J = 126$, C(4), C(3)). CI-MS ($NH_3$): 70 (27), 81 (38), 95 (30), 111 (28), 125 (20), 153 (25), 167 (37), 185 (48), 203 (28), 221 (100), 238 (44).

*(1*RS*,2*RS*,3*SR*,4*RS*,6*SR*)-2-Hydroxy-5-oxo-7-oxabicyclo[4.1.0]heptane-2,3,4-trimethyl Triacetate* ((±)-**56**). As described for (±)-**51**, from (±)-**54** (22 mg, 0.064 mmol): 21 mg (99%) of (±)-**56**. Colorless, unstable oil. $R_f$ (AcOEt/PET 2 : 1) 0.20. IR (film): 2960, 1745, 1565, 1440, 1370, 1230, 1140, 1040, 980, 900, 740. $^1$H-NMR (250 MHz, $CDCl_3$): 4.50 (*dd*, $^2J = 11.9$, $^3J = 5.8$, 1 H); 4.38, 4.28 (2*d*, $^2J = 11.8$, $CH_2$–C(2)); 4.27 (*dd*, $^2J = 12.9$, $^3J = 3.9$, 1 H); 4.14 (*dd*, $^2J = 11.9$, $^3J = 7.7$, 1 H, $CH_2$–C(4)); 3.96 (*dd*, $^2J = 12.9$, $^3J = 3.3$, 1 H, $CH_2$–C(3)); 3.56 (*dd*, $^3J = 3.8$, $^4J = 1.3$, H–C(1)); 3.48 (*d*, $^3J = 3.8$, H–C(6)); 3.47 (*ddd*, $^3J = 7.7$, 5.8, 5.0, H–C(4)); 3.21 (*s*, OH); 2.53 (*dddd*, $^3J = 5.0$, 3.9, 3.3, $^4J = 1.3$, H–C(3)); 2.17, 2.05, 1.98 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 203.0 (*s*, C(5)); 170.6 (*s*, C=O); 69.3 (*s*, C(2)); 66.9, 59.7, 59.6 (3*t*, $J = 147$, 148, 148, 3 $CH_2$); 60.4 (*d*, $J = 182$, C(6)); 56.5 (*d*, $J = 187$, C(1)); 47.7 (*d*, $J = 131$, C(4)); 40.2 (*d*, $J = 129$, C(3)); 20.8, 20.4 (2*q*, $J = 130$, 3 Me). CI-MS ($NH_3$): 81 (42), 94 (37), 107 (52), 123 (96), 164 (100), 195 (19), 211 (27), 225 (21), 248 (4), 267 (46), 285 (11), 302 (1), 327 (13), 262 (2).

*(1*RS*,2*SR*,3*RS*,4*SR*,5*SR*,6*SR*)-6-Acetoxy-5-bromo-1,4-dihydroxycyclohexane-1,2,3-trimethyl Triacetate* ((±)-**57**). A mixture of (±)-**53** (21 mg, 0.049 mmol), pyridine (0.5 ml), and $Ac_2O$ (0.25 ml) was stirred at 20° for 30 min. Toluene (5 ml) was added, and the solvents were evaporated. The residue was purified by FC (silica gel; AcOEt/PET 2 : 1): 21.5 mg (100%) of (±)-**57**. Beige solid. M.p. 129.5 – 130.5°. IR ($CH_2Cl_2$): 3505, 3480, 3470, 3450, 2970, 2910, 1740, 1735, 1370, 1235, 1090, 1045. $^1$H-NMR (250 MHz, $CDCl_3$): 5.48 (*d*, $^3J = 10.7$, H–C(6)); 4.50 (*dd*, $^3J = 10.7$, 2.7, H–C(5)); 4.43 (*dd*, $^2J = 11.1$, $^3J = 6.0$, 1 H); 4.41 (*dd*, $^2J = 12.5$, $^3J = 2.5$, 1 H); 4.30 (*dd*, $^2J = 11.1$, $^3J = 5.7$, 1 H, $CH_2$–C(3)); 4.17 (*dd*, $^2J = 12.5$, $^3J = 8.5$, 1 H, $CH_2$–C(2)); 4.15 (*dd*, $^3J = 2.7$, 5.8, H–C(4)); 4.14 (*s*, OH–C(1)); 2.69 (*dddd*, $^3J = 6.0$, 5.7, 5.8, 4.0, H–C(3)); 2.62 (*s*, OH–C(4)); 2.39 (*ddd*, $^3J = 8.5$, 4.0, 2.5, H–C(2)); 2.17, 2.09, 2.08, 2.02 (4*s*, 4 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.9, 168.9 (2*s*, C=O); 75.7 (*s*, C(1)); 71.3 (*d*, $J = 149$, C(6)); 70.4 (*d*, $J = 149$, C(4)); 66.5 (*t*, $J = 148$, $CH_2$–C(1)); 63.1, 61.7 (2*t*, $J = 140$, $CH_2$); 57.5 (*d*, $J = 155$, C(5)); 43.4, 37.7 (2*d*, $J = 134$, 136, C(2), C(3)); 20.9, 20.8 (2*q*, $J = 129$, 4 Me). CI-MS ($NH_3$): 91 (56), 135 (74), 209 (100), 251 (60), 277 (9), 311 (95), 335 (16), 337 (15), 393 (23), 391 (22). Anal. calc. for $C_{17}H_{25}BrO_{10}$ (469.29): C 43.51, H 5.37, Br 17.03; found: C 43.52, H 5.43, Br 17.08.

*(1*RS*,2*SR*,3*RS*,4*SR*,5*SR*,6*SR*)-4,6-Diacetoxy-5-bromo-1-hydroxycyclohexane-1,2,3-trimethyl Triacetate ((*±)-**58**). A mixture of (±)-**53** (15 mg, 0.035 mmol), pyridine (0.25 ml), and $Ac_2O$ (0.25 ml) was stirred at 20° for 1 d. Toluene (5 ml) was added, and the solvents were evaporated. The residue was purified by FC (silica gel; AcOEt/PET 1 : 1): 18 mg (100%) of (±)-**57**. Colorless oil. $R_f$ (AcOEt/PET 2 : 1) 0.40. IR ($CH_2Cl_2$): 2970, 2925, 2850, 2790, 1750, 1745, 1735, 1720, 1710, 1560, 1460, 1370, 1225, 1045, 1385. $^1$H-NMR (250 MHz, $CDCl_3$): 5.66 (br. *dd*, $^3J = 3.4$, 2.4, H–C(4)); 5.40 (*d*, $^3J = 10.9$, H–C(6)); 4.48 (*dd*, $^3J = 10.9$, 3.4, H–C(5)); 4.34 (*dd*, $^2J = 12.6$, $^3J = 4.3$, 1 H); 4.20, 4.12 (2*d*, $^2J = 12.1$, $CH_2$–C(1)); 4.15 (*dd*, $^2J = 12.6$, $^3J = 7.9$, 1 H, $CH_2$–C(2)); 4.19 – 4.07 (*d*, $^3J = 7.0$, $CH_2$–C(3)); 2.70 (*s*, OH–C(1)); 2.87 (*tdd*, $^3J = 7.0$, 4.8, 2.4, H–C(3)); 2.43 (*ddd*, $^3J = 7.9$, 4.8, 4.3, H–C(2)); 2.18, 2.17, 2.11, 2.08, 2.04 (5*s*, 5 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.6 – 169.4 (*m*, C=O); 75.3 (*m*, C(1)); 71.7, 70.6 (2*d*, $J = 153$, 159, C(5), C(6)); 66.5 (*t*, $J = 149$, $CH_2$–C(1)); 62.1, 61.1 (2*t*, $J = 149$, 147, 2 $CH_2$); 51.0 (*d*, $J = 153$, C(5)); 43.1, 37.0 (2*d*, $J = 137$, 132, C(2), C(3)); 20.7 – 20.8 (5*q*, $J = 130$, 5 Me). CI-MS ($NH_3$): 91 (2), 149 (4), 209 (8), 251 (4), 311 (6), 451 (91), 391 (22), 495 (36), 530 (100). Anal. calc. for $C_{19}H_{27}BrO_{11}$ (511.32): C 44.63, H 5.32; found: C 44.48, H 5.26.

*(1*RS*,2*SR*,3*RS*,4*SR*,5*SR*,6*SR*)-5-Bromo-1,4,6-trihydroxycyclohexane-1,2,3-trimethanol* ((±)-**59**). Gaseous $NH_3$ was bubbled through a soln. of (±)-**53** in anh. MeOH (1.5 ml) and the soln. stirred at 20° for 18 h (TLC control, AcOEt/MeOH 8 : 1). MeOH was evaporated giving (±)-**59** (100%) contaminated with acetamide. FC (silica gel; AcOEt/MeOH 4 : 1) gave 27.3 mg (86%) of pure (±)-**59**. White solid. M.p. 174 – 175°. $R_f$ (AcOEt/MeOH 4 : 1) 0.19. IR (KBr): 3490, 3230, 2885, 1460, 1385, 1360, 1275, 1250, 1175, 1050, 1035, 995, 915, 720, 660, 535. $^1$H-NMR (400 MHz, $CD_3OD$): 4.31 (br. *d*, $^3J = 10.9$, H–C(6)); 4.02 (*s*, H–C(4)); 3.87 (*d*, $^3J = 10.9$, H–C(5)); 3.80, 3.69 (2*d*, $^2J = 11.6$, $CH_2$–C(1)); 3.73 (*d*, $^2J = 11.2$, 1 H); 3.66 (*d*, $^2J = 11.1$, 1 H); 3.58 (*dd*, $^2J = 11.2$, $^3J = 6.4$, 1 H, $CH_2$–C(3)); 3.52 (*dd*, $^2J = 11.1$, $^3J = 5.6$, 1 H, $CH_2$–C(2)); 2.42 (br. *m*, $^3J = 6.4$, H–C(3)); 2.11 (br. *m*, $^3J = 5.6$, H–C(2)). $^{13}$C-NMR (100.6 MHz, $CD_3OD$): 78.4 (*s*, C(1)); 72.5, 71.0 (2*d*, $J = 147$, 150, C(4), C(6)); 66.8 (*t*, $J = 141$, $CH_2$–C(1)); 63.8 (*d*, $J = 150$, C(5)); 62.4, 59.6 (2*t*, $J = 145$, 149, 2 $CH_2$); 45.6, 42.5 (2*d*, $J = 127$, 126, C(2), C(3)). CI-MS ($NH_3$): 81 (78), 91 (100), 107 (56), 123 (43), 135 (22), 149 (17), 167 (35), 185 (13), 229 (7), 285 (3), 283 (3). Anal. calc. for $C_9H_{17}BrO_6$ (301.13): C 35.90, H 5.69; found: C 35.96, H 5.73.

*(1*RS*,2*SR*,3*RS*,4*SR*,5*RS*)-4-Acetoxy-5-bromo-3-hydroxy-6-oxocyclohexane-1,2,3-trimethyl Triacetate* ((±)-**60**). As described for (±)-**51**, from (±)-**57** (25 mg, 0.053 mmol): 24 mg (99%) of (±)-**60**. Colorless oil. $R_f$

(AcOEt/PET 2 : 1) 0.35. IR (film): 2925, 1745, 1370, 1240, 1115, 1090, 1045, 910. $^1$H-NMR (250 MHz, $CDCl_3$): 5.63 (*d*, $^3J=10.3$, H−C(4)); 4.90 (*d*, $^3J=10.3$, H−C(5)); 4.61 (*dd*, $^2J=11.8$, $^3J=6.3$, 1 H); 4.34 (*dd*, $^2J=11.8$, $^3J=3.2$, 1 H); 4.33, 4.15 (2*d*, $^2J=12.5$, $CH_2$−C(3)); 4.11 (*dd*, $^2J=11.8$, $^3J=8.1$, 1 H, $CH_2$−C(1)); 4.08 (*dd*, $^2J=11.8$, $^3J=1.3$, 1 H, $CH_2$−C(2)); 3.61 (*ddd*, $^3J=8.1$, 6.5, 6.3, H−C(1)); 3.19 (*s*, OH); 2.63 (*ddd*, $^3J=6.5$, 3.2, 1.3, H−C(2)); 2.21, 2.11, 2.06, 2.01 (4*s*, 4 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 195.7 (*s*, C(6)); 169.4, 169.7, 170.9, 170.7 (4*s*, C=O); 75.2 (*s*, C(3)); 76.5 (*d*, $J=155$, C(4)); 65.9, 60.2, 58.9 (3*t*, $J=149$, 3 $CH_2$); 57.0 (*d*, $J=148$, C(5)); 43.9 (*d*, $J=129$, C(1)); 42.7 (*d*, $J=133$, C(2)); 20.8, 20.7, 20.5, 20.4 (4*q*, $J=130$, 4 Me). CI-MS ($NH_3$): 84 (100), 107 (28), 135 (33), 157 (44), 215 (46), 267 (28), 311 (14), 391 (3). Anal. calc. for $C_{17}H_{23}BrO_{10}$ (467.27): C 43.69, H 4.96; found: C 43.67, H 4.92.

*(1RS,2RS,5SR,6SR)-4,5,6-Tris(acetoxymethyl)-2-azidocyclohex-3-en-1-yl 4-Nitrobenzoate* ((±)-**61**). A mixture of (±)-**38** (262 mg, 0.741 mmol), anh. $CH_2Cl_2$ (0.7 ml), anh. pyridine (0.3 ml), and 4-nitrobenzoyl chloride (206 mg, 1.11 mmol) was stirred under Ar at 20° for 12 h. It was then diluted with $CH_2Cl_2$ (500 ml) and washed with $H_2O$ (100 ml). The org. phase was dried ($MgSO_4$) and evaporated with toluene and the residue purified by FC (silica gel; AcOEt/PET 1 : 2): 360 mg (100%) of (±)-**61**. Colorless, unstable oil that partially crystallized in the freezer. $R_f$ (AcOEt/PET 2 : 1) 0.54. IR (film): 3115, 2960, 2105, 1740, 1610, 1530, 1370, 1350, 1270, 1235, 1095, 1040, 875, 720, 665. $^1$H-NMR (400 MHz, $CDCl_3$): 8.30, 8.17 (2*d*, $^3J=8.9$, 4 arom. H); 5.84 (br. *d*, $^3J=4.0$, H−C(3)); 5.32 (*dd*, $^3J=4.0$, 3.0, H−C(1)); 4.70, 4.66 (2*d*, $^2J=13.9$, $CH_2$−C(4)); 4.36 (*dd*, $^2J=11.5$, $^3J=6.5$, 1 H); 4.33 (*dd*, $^2J=12.5$, $^3J=6.4$, 1 H); 4.30 (*dd*, $^2J=12.5$, $^3J=6.5$, 1 H, $CH_2$−C(6)); 4.24 (*dd*, $^2J=11.5$, $^3J=6.6$, 1 H, $CH_2$−C(5)); 4.19 (br. *t*, $^3J=4.0$, H−C(2)); 2.93 (br. *ddd*, $^3J=6.6$, 6.5, 6.0, H−C(5)); 2.61 (*dddd*, $^3J=6.5$, 6.4, 6.0, 3.0, H−C(6)); 2.11, 2.06, 2.03 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.6, 170.5, 170.3 (3*s*, C=O); 164.0 (*s*, C=O); 150.8 (*s*); 138.7 (*s*); 134.5 (*d*, $^3J=7.8$, C(4)); 130.8, 123.7 (2*d*, $J=169$, 172, 2 arom. C); 121.5 (*d*, $J=157$, C(3)); 73.0 (*d*, $J=155$, C(1)); 65.1 (*t*, $J=146$, $CH_2$−C(4)); 64.0, 61.2 (2*t*, $J=148$, 149, 2 $CH_2$); 57.6 (*d*, $J=149$, C(2)); 36.7 (*d*, $J=128$, C(5)); 36.4 (*d*, $J=130$, C(6)); 20.78, 20.75, 20.73 (3*q*, $J=130$, 3 Me). CI-MS ($NH_3$): 76 (31), 104 (57), 150 (100), 189 (9), 296 (5), 342 (1), 402 (3), 462 (4).

*(1RS,2SR,3RS,4SR,5RS,6RS)- and (1RS,2RS,3SR,4RS,5SR,6RS)-4,5,6-Tris(acetoxymethyl)-2-azido-7-oxabicyclo[4.1.0]hept-3-yl 4-Nitrobenzoate* ((±)-**62** and (±)-**63**, resp.). A mixture of (±)-**61** (112 mg, 0.228 mmol), $CH_2Cl_2$ (1 ml), and *m*CPBA (95%, *Fluka*; 39.4 mg, 0.228 mmol) was stirred at 40° for 28 h. The soln. was then diluted with $CH_2Cl_2$ (150 ml) and washed rapidly with a cooled aq. sat. $Na_2S_2O_3$ soln. (30 ml) and with aq. sat. $NaHCO_3$ soln. (50 ml). The org. phase was dried ($MgSO_4$) and evaporated. The residue containing two epoxides ('*anti*'/'*syn*'/3.6 : 1) was purified by FC (*Florisil*; AcOEt/PET 1 : 2, 10°): 52.4 mg (46%) of (±)-**62**, 23 mg (20%) of a mixture and 2 mg (2%) of minor isomer (±)-**63**.

*Data of* (±)-**62**: Colorless oil. $R_f$ (AcOEt/PET 2 : 1) 0.54. UV (MeCN): 264 (9800), 257 (10500), 202 (8100). IR (film): 3115, 2965, 2110, 1740, 1610, 1530, 1435, 1370, 1350, 1320, 1270, 1240, 1100, 1040, 1015, 875, 720, 665. $^1$H-NMR (400 MHz, $CDCl_3$): 8.34, 8.21 (2*d*, $^2J=9.0$, 4 arom. H); 5.16 (*dd*, $^3J=4.9$, 3.0, H−C(3)); 4.53 (*dd*, $^2J=11.3$, $^3J=7.7$, 1 H); 4.34 (*dd*, $^2J=11.3$, $^3J=6.4$, 1 H, $CH_2$−C(4)); 4.35, 4.20 (2*d*, $^2J=12.0$, $CH_2$−C(6)); 4.23 (*dd*, $^2J=11.5$, $^3J=5.7$, 1 H); 4.19 (*dd*, $^2J=11.5$, $^3J=6.3$, 1 H, $CH_2$−C(5)); 4.20 (*d*, $^3J=4.9$, H−C(2)); 3.31 (*s*, H−C(1)); 2.78 (*ddd*, $^3J=7.0$, 6.3, 5.7, H−C(5)); 2.52 (*dddd*, $^3J=7.7$, 7.0, 6.4, 3.0, H−C(4)); 2.13, 2.11, 1.99 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.5, 170.2, 164.0 (3*s*, C=O); 150.9 (*s*, C−$NO_2$); 134.4 (*s*, arom. C); 130.9, 123.8 (2*d*, $J=169$, 172, 2 arom. C); 72.5 (*d*, $J=151$, C(3)); 64.7 (*t*, $J=150$, $CH_2$−C(6)); 62.2, 60.9 (2*t*, $J=150$, 152, 2 $CH_2$); 59.4 (*s*, C(6)); 57.3 (*d*, $J=186$, C(1)); 56.9 (*d*, $J=146$, C(2)); 34.9, 34.6 (2*d*, $J=134$, 132, C(4), C(5)); 20.9, 20.7, 20.6 (3*q*, $J=130$, 3 Me). CI-MS ($NH_3$): 76 (40), 104 (54), 150 (100), 210 (2), 299 (2). Anal. calc. for $C_{22}H_{24}N_3O_{10}$ (506.44): C 50.77, H 4.65; found: C 50.62, H 4.54.

*Data of* (±)-**63**: White solid, $R_f$ (AcOEt/PET 2 : 1) 0.50. $^1$H-NMR (400 MHz, $CDCl_3$): 8.35, 8.22 (2*d*, $^3J=8.6$, 4 arom. H); 5.23 (*dd*, $^3J=4.3$, 3.6, H−C(3)); 4.44, 4.16 (2*d*, $^2J=12.4$, $CH_2$−C(6)); 4.39–4.37 (*m*, $CH_2$); 4.28 (*dd*, $^2J=11.7$, $^3J=6.8$, 1 H); 4.22 (*dd*, $^2J=11.7$, $^3J=5.6$, 1 H, $CH_2$); 3.97 (*dd*, $^3J=4.3$, 3.1, H−C(2)); 3.48 (*d*, $^3J=3.1$, H−C(1)); 2.84 (*ddd*, $^3J=6.8$, 6.0, 5.6, H−C(5)); 2.71 (*m*, $^3J=6.0$, 3.6, H−C(4)); 2.13, 2.09, 2.08 (3*s*, 3 Me). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 170.5, 170.4, 170.1 (3*s*, C=O); 163.8 (*s*, C=O); 150.9 (*s*, C−$NO_2$); 134.1 (*s*, arom. C); 130.9, 123.9, 123.8 (3*d*, $J=169$, 172, 172, 3 arom. C); 72.6 (*d*, $J=152$, C(3)); 64.3 (*t*, $J=148$, $CH_2$−C(6)); 62.3, 60.9 (2*t*, $J=143$, 142, 2 $CH_2$); 60.4 (*s*, C(6)); 58.9 (*d*, $J=142$, C(2)); 56.7 (*d*, $J=181$, C(1)); 36.4, 35.4 (2*d*, $J=133$, C(5), C(4)); 20.8, 20.7, 20.6 (3*q*, $J=130$, 3 Me). CI-MS ($NH_3$): 71 (93), 104 (82), 150 (100), 220 (6), 312 (2). Anal. calc. for $C_{22}H_{24}N_3O_{11}$ (506.44): C 50.77, H 4.65; found: C 50.61, H 4.57.

*(1RS,2RS,3SR,4RS,5SR,6RS)-5-Azido-4-hydroxy-7-oxabicyclo[4.1.0]heptane-1,2,3-trimethanol* ((±)-**64**). Gaseous $NH_3$ was bubbled through a soln. of (±)-**62** (88 mg, 0.179 mmol) in anh. MeOH (4 ml) cooled to 0°. The soln. was stirred at 20° for 20 h. MeOH was evaporated and the residue purified by FC (*Florisil*, $CH_2Cl_2$, then AcOEt, then AcOEt/MeOH 8 : 1): 37.7 mg (84%) of (±)-**64**. Colorless oil. $R_f$ (AcOEt/MeOH 8 : 1) 0.11. IR (film): 3330, 2920, 2110, 1660, 1435, 1255, 1050, 665. $^1$H-NMR (400 MHz, $CD_3OD$): 3.92 (*dd*, $^2J=11.2$,

$^3J$ = 6.1, 1 H of $CH_2$−C(2)); 3.86 – 3.82 (4 H, 1 H of $CH_2$−C(2), $CH_2$−C(3), H−C(5)); 3.73 (*dd*, $^3J$ = 7.4, 3.6, H−C(4)); 3.76, 3.53 (2*d*, $^2J$ = 12.4, $CH_2$−C(1)); 3.14 (*s*, H−C(6)); 2.53 (*td*, $^3J$ = 6.2, 6.1, H−C(2)); 2.17 (*dtd*, $^3J$ = 6.4, 6.2, 3.6, H−C(3)). $^{13}$C-NMR (100.6 MHz, $CD_3OD$): 72.8 (*d*, *J* = 145, C(4)); 64.2 (*t*, *J* = 143, $CH_2$−C(1)); 63.3 (*s*, C(1)); 61.8 (*d*, *J* = 145, C(6)); 60.8, 60.4 (2*t*, *J* = 143, 2 $CH_2$); 58.7 (*d*, *J* = 179, C(5)); 42.1, 39.4 (2*d*, *J* = 128, 125, C(2), C(3)). CI-MS ($NH_3$): 81 (89), 95 (100), 107 (52), 122 (68), 138 (15), 167 (3). Anal. calc. for $C_9H_{15}N_3O_5$ (245.23): C 44.08, H 6.17, N 17.13; found: C 44.09, H 6.19, N 17.01.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*RS*)-5-Amino-1,4-dihydroxycyclohexane-1,2,3-trimethanol* ((±)-**65**). A mixture of (±)-**64** (9 mg, 0.036 mmol), MeOH (1 ml), and 20% $Pd(OH)_2$ on charcoal (4 mg) was degassed and shaken overnight under $H_2$ at 20°. The soln. was then filtered through a *Celite* pad and evaporated: 8 mg (98%) of (±)-**65**. For further purification, the residue was dissolved in 1N HCl in MeOH/$H_2O$ 1 : 1 (0.1 ml) and loaded onto *Dowex-50WX8* ($H^+$ form). The resin was washed with $H_2O$ (10 ml) and MeOH (10 ml), then eluted with 5% aq. $NH_3$. Evaporation of the alkaline fractions: 7.3 mg (90%) of pure (±)-**65**. Colorless oil. IR (film): 3290, 2940, 2865, 1740, 1650, 1465, 1435, 1385, 1295, 1255, 1220, 1130, 1085, 1050, 1025, 835, 780, 675. $^1$H-NMR (400 MHz, $D_2O$): 3.83 (*dd*, $^2J$ = 12.1, $^3J$ = 3.5, 1 H); 3.79 (*dd*, $^2J$ = 11.5, $^3J$ = 5.4, 1 H); 3.78 (*dd*, $^2J$ = 12.1, $^3J$ = 6.0, 1 H, $CH_2$−C(3)); 3.63 (*dd*, $^2J$ = 11.5, $^3J$ = 8.0, 1 H, $CH_2$−C(2)); 3.57 (*dd*, $^3J$ = 10.4, 5.4, H−C(4)); 3.44, 3.37 (2*d*, $^2J$ = 11.6, $CH_2$−C(1)); 3.29 (*ddd*, $^3J$ = 13.0, 10.4, 3.7, H−C(5)); 2.34 (*dtd*, $^3J$ = 6.0, 5.4, 3.5, H−C(3)); 1.95 (*dt*, $^3J$ = 8.0, 5.4, H−C(2)); 1.84 (*dd*, $^2J$ = 13.0, $^3J$ = 3.7, $H_\alpha$−C(6)); 1.48 (*t*, $^2J$ = 13.0, $H_\beta$−C(6)). $^{13}$C-NMR (100.6 MHz, $D_2O$): 77.4 (*s*, C(1)); 75.4 (*d*, *J* = 147, C(4)); 69.2 (*t*, *J* = 142, $CH_2$−C(1)); 61.4, 59.8 (2*t*, *J* = 142, 141, 2 $CH_2$); 50.5 (*d*, *J* = 143, C(5)); 45.8, 44.9 (2*d*, *J* = 122, 131, C(2), C(3)); 41.8 (*t*, *J* = 128, C(6)). CI-MS ($NH_3$): 83 (24), 106 (100), 120 (36), 136 (17), 154 (50), 172 (88), 186 (3), 202 (1), 222 (5). Elemental analysis, see (±)-**66**.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*RS*)-5-Acetamido-4-acetoxy-1-hydroxycyclohexane-1,2,3-trimethyl Triacetate* ((±)-**66**). A mixture of (±)-**65** (11 mg, 0.05 mmol), anh. pyridine (50 µl) and $Ac_2O$ (50 µl) was stirred at 20° for 24 h. Solvent evaporation and FC (silica gel; AcOEt): 17.4 mg (81%) of (±)-**66**. Colorless oil. $R_f$ (AcOEt) 0.057. IR (film): 3360, 2925, 1740, 1660, 1650, 1555, 1435, 1370, 1240, 1130, 1040, 905, 730. $^1$H-NMR (400 MHz, $CDCl_3$): 5.69 (*d*, $^3J$ = 8.1, NH); 4.83 (*dd*, $^3J$ = 11.4, 5.4, H−C(4)); 4.53 (*dd*, $^2J$ = 12.2, $^3J$ = 4.4); 4.43 (*dd*, $^2J$ = 12.2, $^3J$ = 5.8, $CH_2$−C(3)); 4.40 (*dddd*, $^3J$ = 11.7, 11.4, 8.1, 4.5, H−C(5)); 4.36 (*dd*, $^2J$ = 11.7, $^3J$ = 6.7, 1 H); 4.29 (*dd*, $^2J$ = 11.7, $^3J$ = 6.4, 1 H, $CH_2$−C(2)); 4.04, 3.97 (2*d*, $^2J$ = 11.3, $CH_2$−C(1)); 3.50 (*s*, OH−C(1)); 2.64 (*dddd*, $^3J$ = 5.8, 5.4, 5.0, 4.4, H−C(3)); 2.23 (*dd*, $^2J$ = 13.9, $^3J$ = 4.5, $H_\alpha$−C(6)); 2.10, 2.09, 2.04, 2.02, 1.94 (5*s*, 16 H, Me, H−C(2)); 1.43 (*dd*, $^2J$ = 13.9, $^3J$ = 11.7, $H_\beta$−C(6)). $^{13}$C-NMR (100.6 MHz, $CDCl_3$): 171.7, 170.6, 170.4, 170.1 (4*s*, C=O); 74.5 (*d*, *J* = 154, C(4)); 71.9 (*s*, C(1)); 69.1 (*t*, *J* = 149, $CH_2$−C(1)); 62.2, 61.6 (2*t*, *J* = 150, 149, 2 $CH_2$); 45.4 (*d*, *J* = 148, C(5)); 41.8, 39.6 (2*d*, *J* = 125, 132, C(2), C(3)); 40.9 (*t*, *J* = 127, C(6)); 23.4 (*q*, *J* = 128, 3 Me); 21.1, 21.0, 20.8 (3*q*, *J* = 130, 3 Me). CI-MS ($NH_3$): 72 (100), 191 (41), 233 (79), 298 (45), 338 (13), 372 (18), 432 (48). Anal. calc. for $C_{19}H_{29}NO_{10}$ (431.44): C 52.89, H 6.78; found: C 52.81, H 6.74.

*(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*RS*)-5-Amino-4-hydroxy-7-oxabicyclo[4,1.0]heptane-1,2,3-trimethanol* ((±)-**67**). A suspension of 10% Pd/C (8 mg) in MeOH (1 ml) was shaken for 30 min under $H_2$. After addition of (±)-**64** (8 mg, 0.033 mmol), the suspension was shaken for 5 min and then filtered over a *Celite* pad. The filtrate was evaporated: 7 mg (98%) of (±)-**67** (storage at −28°). Colorless, instable oil. IR (film): 3345, 2895, 1730, 1645, 1460, 1570, 1415, 1245, 1035, 925. $^1$H-NMR (400 MHz, $CD_3OD$): 3.91 (*dd*, $^2J$ = 11.3, $^3J$ = 6.0, 1 H); 3.82 (*dd*, $^2J$ = 11.3, $^3J$ = 6.7, $CH_2$−C(2), 1 H); 3.81 (*dd*, $^2J$ = 10.8, $^3J$ = 7.0, 1 H); 3.77 (*dd*, $^2J$ = 10.8, $^3J$ = 6.0, $CH_2$−C(3)); 3.74, 3.47 (2*d*, $^2J$ = 12.1, $CH_2$−C(1)); 3.46 (*dd*, $^3J$ = 7.1, 3.6, H−C(4)); 3.09 (*d*, $^3J$ = 7.1, H−C(5)); 2.98 (*s*, H−C(6)); 2.52 (*dt*, $^3J$ = 6.7, 6.0, H−C(2)); 2.16 (*dtd*, $^3J$ = 7.0, 6.0, 3.6, H−C(3)). $^{13}$C-NMR (100.6 MHz, $CD_3OD$): 75.0 (*d*, *J* = 141, C(4)); 64.9 (*t*, *J* = 143, $CH_2$−C(1)); 63.2 (*s*, C(1)); 61.4 (*d*, *J* = 176, C(6)); 61.0, 60.7 (2*t*, *J* = 143, 147, 2 $CH_2$); 51.7 (*d*, *J* = 139, C(5)); 41.7, 39.7 (2*d*, *J* = 127, 126, C(2), C(3)). CI-MS ($NH_3$): 70 (24), 77 (55), 91 (100), 107 (72), 121 (45), 135 (21), 147 (10), 188 (10), 201 (3), 220 (3).

*X-Ray Crystal-Structure Determination of (1*RS*,2*RS*,5*SR*,8*SR*)-2-Acetoxy-6-oxabicyclo[3.2.1]oct-3-ene-5,8-dimethyl Diacetate* ((±)-**33**). Crystal data and measurement conditions are given in the *Table*. A colorless, irregular, plate-shaped chip of a larger cystal was mounted. On a *Stoe IPDS* (oscillation 1°, sample-IP distance 70 mm, graphite-monochromatized $\lambda(\mathrm{Mo}K_\alpha)$ 0.71073 Å), 200 images were recorded for 6 min each at *T* 293(2)K. All crystals studied were pseudo-merohedric twins, and the interpretation of the images was carried out with two orientation matrices. Neither decay nor absorption corrections were performed. Solution by direct methods (SHELXTL [46]), refinement with the full matrix and weights $[\sigma^2(F_0^2)]^{-1}$. H-Atoms were refined with IDPs and coordinates, except methyl H-atoms which were made to ride on their C-atoms. Crystallographic data for (±)-**33** have been deposited at the *Cambridge Crystallographic Data Centre* as Supplementary Publication No. CCDC-117983.

Table. *Crystal Data and Structure Refinement of (±)-***33**

| | | | |
|---|---|---|---|
| Empirical formula | $C_{15}H_{20}O_7$ | $\theta$ Range [°] | 2.53 to 24.99 |
| Formula weight | 312.31 | Index ranges | $-9 \leq h \leq 9$, $-10 \leq k \leq 11$, $-14 \leq l \leq 14$ |
| Crystal system | triclinic | Reflect. collected | 5774 |
| Space group | $P\bar{1}$ | Independent reflect. | 2639 ($R$(int) = 0.0234) |
| Unit cell dimensions $a$ [Å] | 8.427(2) | Completeness to $2\theta = 24.99°$ | 91.9% |
| $b$ [Å] | 9.256(2) | Refinement method | Full-matrix least-squares on $F^2$ |
| $c$ [Å] | 11.726(2) | Data/restraints/parameters | 2636/0/243 |
| $\alpha$ [°] | 68.21(3) | Goodness-of-fit on $F^2$ | 4.236 |
| $\beta$ [°] | 81.98(3) | Final $R$ indices ($I > 2\sigma(I)$) | $R_1 = 0.0539$, $wR_2 = 0.0848$ |
| $\gamma$ [°] | 73.10(3) | $R$ indices (all data) | $R_1 = 0.0688$, $wR_2 = 0.0853$ |
| Volume [Å$^3$] | 812.1(3) | Largest difference peak and hole [e · A$^{-3}$] | 0.213 and −0.163 |
| $Z$ | 2 | | |
| Density calc. [Mgm$^{-3}$] | 1.277 | | |
| Absorption coeff. [mm$^{-1}$] | 0.102 | | |
| $F(000)$ | 332 | | |
| Crystal size [mm] | 0.5 × 0.2 × 0.1 | | |

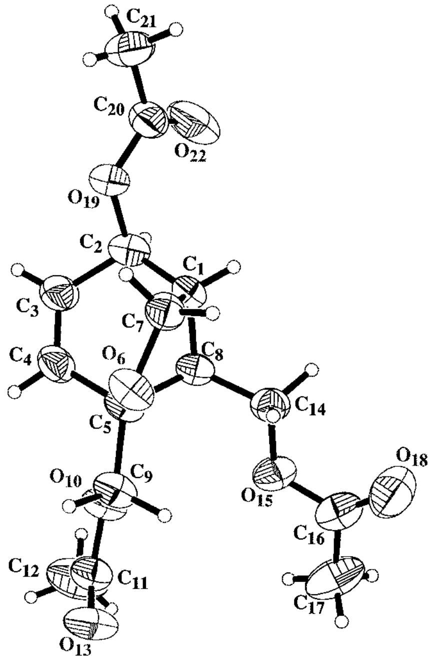

Fig. 1. *ORTEP Representation of (±)-***33** *showing heavy atoms with 50% probability and atom numbering*

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